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Second Progress Report

DIVISION B

NATIONAL DEFENSE RESEARCH COMMITTEE

OF THE

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

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OSRD No. 945

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DIVISION B

NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Report on "Development of Oxygen-Carrying Compounds."
to
September 1, 1942
by
Dr. Harvey Diehl

OSRD No. 945
Serial No. 396
Copy No. 47

Date: October 16, 1942

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TABLE OF CONTENTS

This report is organized as a supplement to our first Progress Report (Report XXVI, Report to N.D.R.C. No. 22); section numbers are therefore not consecutive, the same section number being reserved for the same subject matter. The subscript $_s$ indicates that the material in the section is a continuation of material found in the first Progress Report.

[redacted]

Serial No. 396

DIVISION B

NATIONAL DEFENSE RESEARCH COMMITTEE
of the
OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT
Section B-7

Report on "Development of Oxygen-Carrying Compounds" (NLB-42)

Endorsement (1) From E. P. Stevenson, Chairman, Section B-7, to Roger Adams, Chairman, Division B. Forwarding Report and noting:

"This is the second progress report summarizing chemical investigation of the regenerative oxygen absorbent "Salcomine" and the synthesis and properties of related chemical compounds."

(2) Twenty-five copies forwarded to Dr. Irvin Stewart, Secretary of the National Defense Research Committee, as Progress Report under Contract B-225, OEMsr-215 with Iowa State College.

Roger Adams, Chairman
by Harris M. Chadwell
Technical Aide

TABLE OF CONTENTS

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Section			Page
Part			
	Subsection		

Section	Page

Part

Subsection

Ia. General Statement Regarding Personnel, Working Conditions and Related Activities.

The following changes in the staff working on this project were made during the interval covered by this report. Miss Lois Hanselmeier stopped work on May 20 to be married. Mr. John Mathews, Jr., was added to the staff on June 1, and Mr. Richard Brouns was added June 15. Mr. Guy Gardner, a draftsman, was employed on the project from June 1 to August 10. Mr. Carl Anderson and Mr. Allen Cox, machinists, were employed on an hourly basis at intervals during the summer months. Routine analytical work and some of the more tedious chemical operations were carried out by Mr. W. R. Schwandt, Mr. Ross Curtis and Mr. Francis Statton, working on an hourly basis. The major part of the work described in this report has been carried out by Mr. Clifford Hach, Mr. Lawrence Liggett, Mr. James Head, and Mr. George Harrison.

On June 9th Dr. C. C. Furnas visited the laboratory. Early in July, Dr. Melvin Calvin of the University of California visited the laboratory and the work of the two groups was further correlated. During the latter part of July, Mr. Lawrence Liggett and Mr. James Head visited the various laboratories in the East engaged on this project and returned with an enlarged picture of the problem as a whole and with considerable information valuable to the work being conducted in this laboratory. Dr. S. S. Prentiss and Dr. W. W. Beck visited the laboratory August 26; some time was devoted to a discussion with Dr. Prentiss of the methods of handling reports, and the work at this laboratory was summarized for Dr. Beck who left a number of excellent suggestions for further work.

The administration of Iowa State College has continued to give their whole-hearted support to this work and as the need has arisen has made available further laboratory space and shop facilities. The staff wishes to express its gratitude to the College for this excellent assistance.

II$_a$. General Review and Objective.

The general method of preparing reports in this laboratory was outlined in the corresponding section of out First Progress Report (Report XXVI). The method of preparing detailed reports covering the individual items of the research program has been continued; these reports now number XLVII. A table giving the numbers, authors, content, period covered and date of these reports is given in Appendix I.

The objectives of the present work are largely the same as those outlined in our First Progress Report. The emphasis, however, during this period has been placed on the preparation of new compounds rather than the study of the parent compound. In general the work has been devoted to a study of the derivatives obtained from substituted salicylaldehydes in pursuance of the agreement reached in February with the group at the University of California. In the case of the compounds which have appeared to offer promise, intensive studies of the various properties were made; this is particularly true of di-(2-hydroxy-3-methoxybenzal)ethylenediimino cobalt (Co-Ox M). Some attention has been devoted to a determination of the useful life of this compound but this work has been of a rather preliminary nature in view of the extensive work in this direction being carried out at the Massachusetts Institute of Technology.

III$_a$. General Summary.

(1) The study of cobalt compounds similar in general character to the parent, oxygen-carrying compound but derived from other diamines than ethylenediamine has been extended by a study of two more diamines. None of the compounds prepared functioned as oxygen carriers further substantiating the general statement that substitution into the ethylenediamine portion of the molecule invariably leads to an inactive compound.

(2) The cobalt compound derived from 2-hydroxy-3-methoxybenzaldehyde and ethylenediamine was found to carry oxygen and to oxygenate at a rate approximately twenty times that of the parent compound. This compound was obtained in the form of a hydrate which was converted into the active form by heating in a vacuum at 170°. An extensive study of six methods for the preparation of this compound was made and it was found that the most satisfactory method was that involving the precipitation of the cobalt derivative from a solution of the sodium salt of the Schiff's base in dilute alcohol. The preparation

of the material was carried from the laboratory through pilot plant operation. Certain difficulties involved in the preparation, principally in the activation or dehydration, were overcome. The rate of oxygenation of the compound was determined at various temperatures and the optimum rate of absorption of oxygen from air at atmospheric pressure was found to occur at 5-10°. Unfortunately the compound was found to be extremely hygroscopic and to form a hydrate which did not carry oxygen. An investigation was conducted to establish the relationship between the competing absorption of oxygen and of water at various humidities. The magnetic susceptibility and oxygen pressure of this compound were measured at California.

Two studies of the rate of deterioration of the compound were made. The material deteriorated about 50 per cent faster than the parent compound. The rate of deterioration was much more rapid during the early phases of the test (about 3.0 per cent per 100 cycles) but became much less as the test progressed, the overall rate of deterioration in the first test being 2.1 (2700 cycles) and in the second 1.3 (3000 cycles) per cent per hundred cycles.

(3) The nitration of salicylaldehyde was studied and the following factors were varied in order to find optimum conditions: the concentration of nitric acid, the amount of nitric acid, the amount of acetic acid used as solvent, and the temperature of reaction. An entirely satisfactory procedure was devised for the nitration, for the separation of the 3- and 5-isomers, for the purification of the 2-hydroxy-3-nitrobenzaldehyde for the preparation of its Schiff's base with ethylenediamine, and for the preparation and activation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt. Detailed studies of the activation of di-(2-hydroxy-3-nitrobenzal)-ethylenediimine cobalt showed that a temperature of 120-125° and a vacuum was necessary for rapid activation. The rate of oxygenation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt at various temperatures and humidities in air and oxygen at atmospheric pressure was determined. The rate of oxygenation of the 3-nitro compound is much greater than that of the parent compound. The extent of oxygenation varies markedly with the oxygen pressure. Unlike the parent compound, the rate of oxygenation of the 3-nitro compound is only slightly affected by temperature. The rate of oxygenation of this compound is slightly affected by the humidity of the air, but this advantage is more than offset by the absorption of moisture by the compound, which renders the material inactive. An investigation of the competing absorption of oxygen and of moisture was made by exposing samples of the activated compound to air at various humidities. These studies showed that the amount of oxygen absorbed decreased with increasing moisture content in the air.

(4) The cobalt derivative of 2-hydroxy-3-nitro-5-methylbenzaldehyde and ethylenediamine was prepared. Since the cobalt derivatives of the Schiff's bases of 2-hydroxy-3-nitrobenzaldehyde and of 2-hydroxy-5-methylbenzaldehyde with ethylenediamine had been previously found to carry oxygen, it was a surprise that this compound did not function as an oxygen carrier. The cobalt compound of 2-hydroxy-5-phenylbenzaldehyde and ethylenediamine was prepared and found not to carry oxygen. The cobalt compound of 2-hydroxy-4,6-dimethylbenzaldehyde and of 2,3-dihydroxybenzaldehyde and ethylenediamine were prepared and found not to carry oxygen.

(5) 2-Hydroxy-3-ethoxybenzaldehyde was synthesized successfully from catechol by conversion of the latter to its monoethyl ether and the application of the Duff reaction to the latter. Attempts to prepare this aldehyde by the demethylation of 2-hydroxy-3-methoxybenzaldehyde and ethylation of the 2,3-di-hydroxybenzaldehyde so produced, failed. The aldehyde was also obtained in good yield from a crude material supplied by the Monsanto Chemical Company. The condensation of 2-hydroxy-3-ethoxybenzaldehyde and ethylenediamine was effected and the cobalt derivative of this condensation product prepared by several methods. Di-(2-hydroxy-3-ethoxybenzal)ethylenediimine cobalt, like the corresponding 3-methoxy compound was obtained initially as an inactive hydrate, but unlike the 3-methoxy compound, could be activated at temperatures around 110°. Di-(2-hydroxy-3-ethoxybenzal)ethylenediimine cobalt is far less hygroscopic than the methoxy compound and since its water can be expelled without great difficulty it possesses a marked advantage over the methoxy compound. The rate of oxygenation of di-(2-hydroxy-3-ethoxybenzal)ethylenediimine cobalt was determined in air at atmospheric pressure at various humidities; the rate of oxygenation is only slightly affected by temperature, being about as rapid at 20° as at 0°. The rate of oxygenation of di-(2-hydroxy-3-ethoxybenzal)ethylenediimine cobalt is somewhat slower than that of the 3-methoxy compound, but far faster than that of the parent compound and sufficiently great that oxygenation may be carried out in oxygen-producing apparatus at atmospheric pressure or slightly above.

(6) Di-(2-hydroxy-3-<u>n</u>-propoxybenzal)ethylenediimine cobalt was prepared and a study begun of its properties. The material oxygenates very rapidly but is extremely hygroscopic. Preliminary work was carried out on the synthesis of the following 2-hydroxy-3-alkoxybenzaldehydes: <u>iso</u>-propoxy, <u>n</u>-butoxy, <u>sec</u>-butoxy, <u>tert</u>-butoxy, <u>iso</u>-butoxy, allyloxy, <u>n</u>-amyloxy, and β-ethoxyethoxy.

(7) The compound dibenzoylmethane was synthesized; several attempts by different methods to effect condensation of it with ethylenediamine failed. A cobalt derivative has therefore not been obtained.

(8) Formylcamphor, an β-keto aldehyde capable of existing in enolic form was prepared by a method previously described. This compound was condensed with ethylenediamine and also with o-phenylenediamine and the cobalt derivative of these two Schiff's bases prepared. Neither of these compounds was an oxygen carrier.

(9) Hexa-allylamineperoxodihydroxodicobalt trichloride, a polynuclear compound containing a peroxo bridge, was prepared and found to hold its oxygen so tightly that it was not released at temperatures below the decomposition temperature of the compound.

(10) A differential manometric apparatus was constructed by which the oxygen-carrying capacity of the compounds could be determined at various temperatures and pressures in such a manner that errors due to the loss of oxygen or the absorption of water during the process of weighing involved in the older method are eliminated. Although apparently quite complicated, the apparatus is relatively simple in theory and use, and has been used not only for the determination of oxygen capacity but also the for the determination of the rate of oxygenation of the compounds.

(11) An automatic apparatus for the continous oxygenation and deoxygenation of oxygen-carrying compounds was designed and constructed. This apperatus was of the rotating drum variety and chosen to minimize the temperature to which the material as a whole was heated during the deoxygenation phase of the cycle. Tests on the parent compound and the methoxy compound were made using this apparatus.

(12) Various types of apparatus were constructed for measuring the rate of oxygenation of the compound studied in air and oxygen at various temperatures and humidities.

(13) An apparatus was constructed to manufacture 100 cu. ft. per hour of oxygen of purity of 95+ per cent, using as the oxygen carrier di-(2-hydroxy-3-methoxybenzal) ethylenediimine cobalt (Co-Ox M). the apparatus is of the circulating solid type in which the material moves from an oxygenation chamber, where it is cooled to 5° by mechanical refrigeration and exposed to air at atmospheric pressure, to a deoxygenation chamber where it is heated to 70° and releases its oxygen at slightly lower than atmospheric pressure. The material is moved by four

screw conveyors operating in pipes arranged in a skewed rectangle A unique mechanism was devised to effect the transfer of the solid material from one chamber to the other without contaminating or losing appreciable amounts of the oxygen produced. The deoxygenation is carried out at a slightly higher pressure than the oxygenation and a small amount of oxygen is sacrificed to flush from the solid material any air which would otherwise find its way into the deoxygenation chamber. The apparatus contains about 100 lbs. of Co-Ox M which circulates completely through the apparatus in about 18 minutes. Air dried by passage over potassium hydroxide and magnesium perchlorate is blown through the apparatus by a centrifical blower. The apparatus was designed to operate completely electrically but was modified for alternative operation by a gasoline engine being then completely self contained. At the time this report was written oxygen of 95 per cent purity had been generated at the rate of 35 cubic feet per hour. The deficiency in capacity is due to several causes which are being corrected by modifications in the construction of the apparatus.

V_2. Cobalt Compounds from Diamines other than Ethylanadiamine

The substitution of other diamines for ethylanediamine was dascribed in our first Progreas Report. Without axception the cobalt compounda in which such substitutions were meda ware inactive as oxygen carriars. This work hes now been extanded by studies of the derivativas of tetramethylethylanadiamina and methylonediamine. In both cases tha oroducte ware inactive.

A_2. Propylanadiamine

The failura of the efforts in this laboratory to prepare a successful oxygen-carrying compound from propylanediamine, selicylaldehyda and cobalt waa in marked disagreement with work at California in which an activa material waa preparod. It is now reported by Calvin that the propylenediamine uaod et California containad some ethylonediamina which eccounted for tha aotivity found.

J. Tetramethylethylenadiamine

The highly symmetrically substitutad ethylenediamina, tetramethylathylenediamine, $(CH_3)_2C(NH_2)C(NH_2)(CH_3)_2$, waa obtained from tha Commercial Solvants Corporetion. Its identity and purity were checked and its condensation with salicylaldehyde affectad in absolute alcohol. Tha cobalt derivative of the condensation product was prepared by five methods and numerous attempts wora made to activate the compound by various heat traatmants. Nona of the preparations functionad as an oxygen cerrier.

The praaenca of a nitro or a methoxy group in tha 3-position of salicylaldehyde has been shown to have a beneficiel affect on the propertias of the parant oxygan-carrying compound. It seemed possible that the presence of these groupa might rander the tetramethylethylenediamine compound active and accordingly the cobalt derivatives of the condensation products of 3-nitro and 3-methoxyaalicyleldehyde and tetramethylathylenadiamina were prepared and subjocted to the usual tests. All of the preparations were found to be inactiva, thua further confirming tha general concluaion that veriations in the ethylanediamina portion of the parent compound always leads to a material which ia not an oxygan-cerrier. The detaila of the work on the derivetivos of tetramethylethylonediamine will be found in Report XXXV.

K. Methylenediamine

A sample of methylenediamine hydrochloride was obtained from the du Pont Company and after considerable effort the Schiff's base with salicyladehyde was prepared. In the preliminary work attempts to prepare the Schiff's base by adding sodium hydroxide to a solution of the diamine hydrochloride and salicylaldehyde in absolute alcohol yielded an oil from which only a very small quantity of condensation product could be isolated. The condensation was finally effected with reasonable success by dissolving the methylenediamine hydrochloride in water, cooling to C°, neutralizing the hydrochloric acid with a cold solution of sodium hydroxide and then quickly adding the cold solution of methylenediamine to a solution of salicylaldehyde in alcohol. By this technique a respectable yield of Schiff's base resulted. M.p.: 132°.

Preparation of the cobalt derivative of disalicylalethylenediimine was prepared by means of the sodium salt of the Schiff's base and by the alcohol method. Both preparations yielded a yellow colored cobalt derivative which was at first thought to be cobalt salicylaldehyde. This assumption was found to be erroneous as analysis for cobalt and nitrogen proved the material to be the desired compound. Unfortunately, however, this compound showed no oxygen activity upon being subjected to the usual tests.

VI$_a$. Cobalt Compounds from Substituted Salicylaldehydes and Similar Carbonyl Compounds and Ethylenediamine

B$_a$. 2-Hydroxy-3-methoxybenzaldehyde

(Co-Ox M)

(1) <u>General Summary of Work on this Compound to Date</u>. The discovery that the aldehyde 2-hydroxy-3-methoxybenzaldehyde formed a compound with ethylenediamine and cobalt that showed the same general properties as the parent compound prepared from salicylaldehyde, ethylenediamine and cobalt, but having a much more rapid rate of oxygenation, lead to an intensive investigation of this compound. The rapid rate of oxygenation of this material at atmospheric pressure in dry air is a most important advantage over other compounds previously developed since it makes possible a reduction in the time required per cycle and renders feasible apparatus not requiring high pressure air.

The methods of synthesizing this material, di-(2-hydroxy-3-methoxybenzal) ethylenediimine cobalt, were studied exhaustively and the most satisfactory method of preparation was carried from the laboratory through pilot plant production. All of the factors involved in the synthesis were studied, and, as with the parent compound, the troubles were eliminated and the conditions so well established that no difficulty should be experienced in the adaptation of the procedure to the preparation of larger amounts by the Rumford Chemical Works.

The rate of oxygenation of the material at various temperatures was determined. Some studies on the rate of deterioration of the compound in use were made and the hygroscopic character of the compound was carefully studied. The magnetic susceptibility of the material and its oxygen pressure at various temperatures were measured by Calvin at California.

The material was used successfully to produce oxygen in a machine designed expressly to take advantage of the unique characteristics of the material (see Section XI of this report).

Fortunately large quantities of 2-hydroxy-3-methoxybenzaldehyde appear to be available (Monsanto Chemical Company).

The work on di-(2-hydroxy-3-methoxybenzal) ethylenediimine cobalt is reported in detail in Reports XVII, XXVII, XXXII and XXXVIII and is summarized in the following subsection of this report.

(2) The Schiff's Base Di-(2-hydroxy-3-methoxybenzal)ethylenediimine. Numerous preparations of the above Schiff's base used throughout the investigation of its cobalt derivative were obtained by the condensation of 2-hydroxy-3-methoxybenzaldehyde and ethylenediamine. The reaction was generally carried out in hot alcohol medium from which the Schiff's base precipitates as a bright yellow crystalline material. The Schiff's base may be recrystallized from hot absolute alcohol or from ether. The m.p. following careful purification was found to be 161°. Di-(2-hydroxy-3-methoxybenzal)ethylenediimine is readily soluble in warm caustic solution. Recrystallization of this material is not necessary in the preparation of a satisfactory oxygen-carrying material. Indeed, in the procedure finally recommended, this base after being formed is not filtered and isolated but dissolved and used directly. Conditions were determined for precipitating it in a form which can be readily dissolved in dilute alkali.

(3) Chemical Characteristics of Di-(2-hydroxy-3-methoxybenzal)-ethylenediimine Cobalt. (Co-OxM). The cobalt derivative of the Schiff's base di-(2-hydroxy-3-methoxybenzal)ethylenediimine may be prepared in a variety of ways which will be presented in subsection (5). This compound, when first precipitated from a medium in which water is present, is obtained in a hydrated

form which shows no ability to absorb oxygen. In order to convert the hydrate into the active, oxygen-carrying material, the material must be activated. The procedure usually employed was to subject the material to a temperature of 160-170° under a vacuum. In the activation process a definite amount of water is lost, about 4.5 per cent, corresponding to one molecule of water per cobalt atom (theoretical 4.68 per cent). The resulting material has been shown to absorb 4.15 per cent of oxygen which corresponds to the theoretical structure which was presented for this type of compound.

This compound has been shown to be remarkably stable at a temperature of 170° in a vacuum; short periods of time at a temperature of 200° produces only a slight decomposition. The active material in both the oxygenated and deoxygenated form shows remarkable affinity for moisture. It is so hygroscopic that to accurately weigh the material in air is a difficult task.

As with the parent compound, this material is a fine dusty powder which is extremely irratating to the lungs.

(4) Determination of the Oxygen-Carrying Capacity by a Volumetric Method. In view of the controversy that has arisen at various times in regard to the determination of the oxygen carrying capacity of these materials, a method was devised by which the determination could be made by the volumetric measurement of the oxygen evolved from the compounds and errors inherent to the gravimetric method eliminated.

The apparatus designed for the determination of oxygen-carrying capacity consisted of a source of carbon dioxide, a drying train, a glass tube in which the boat of material was placed, and a nitrometer. Dry ice was used as a source of carbon dioxide and the dry ice container was connected with a pressure regulator to control the rate of flow through the apparatus to the nitrometer. The carbon dioxide gas evolved from the dry ice was passed through a U-tube containing phosphorous pentoxide on asbestos. This was found essential since the dry ice always contained moisture condensed on its surface which was carried off with the carbon dioxide gas and formed ice in the tube containing the boat at low temperature. The procedure employed in determining the capacity of a sample using this apparatus was the following. A sample of the compound was deoxygenated under a vacuum at 100° and then the boat placed in a vacuum desiccator which was immediately evacuated before the boat had cooled appreciably. After cooling to room temperature the vacuum was quickly released and the boat of deoxygenated compound weighed immediately. This weighing was made by first placing the approximate weights on the balance as determined by previous weighing, so that only about 15 seconds were required to obtain the final weight. This sample was oxygenated in a bomb under 200 pounds oxygen pressure for 15 minutes, and then weighed immediately after removing from the bomb. The boat was then placed in the deoxygenation tube of the capacity apparatus and the tube closed. The tube containing the boat was surrounded by dry ice and then carbon dioxide passed over the boat containing the compound until all the air had been swept out as shown by micro-bubbles in the nitrometer. The nitrometer was filled with 36 per cent potassium hydroxide containing a trace of barium chloride added to prevent the formation of foam in the top of the nitrometer. The oxygen in the sample was released and collected in the nitrometer by first removing the dry ice packing and then gradually heating the tube containing the boat of sample with an infra-red lamp. The tube was swept out with carbon dioxide until micro-bubbles were obtained. The capacity of the sample was calculated from the volume of oxygen collected as will be subsequently shown. After cooling to room temperature in an atmosphere of carbon dioxide, the boat containing the deoxygenated sample was again weighed in order to serve as a comparison for the volumetric method.

It was found that the completely oxygenated methoxy compound lost oxygen slowly at room temperature under atmospheric pressure. Under a diminished oxygen pressure, produced either by a vacuum or a stream of carbon dioxide, it evolves a large portion of its absorbed oxygen. It was also found that the parent compound upon being placed in the above described capacity apparatus lost weight slowly in an atmosphere of carbon dioxide. Because of these observations it was found necessary to cool the tube containing the weighed sample of oxygenated material with dry ice so that the compounds would retain their absorbed oxygen until the air present in the tube at the time of the introduction of the sample was completel. swept out.

Since the oxygen collected was measured over a potassium hydroxide solution, correction was made for the vapor pressure of the solution as follows: from the International Critical Tables, Vol. III, page 528, the formula given for calculating the vapor pressure of aqueous solutions was

$$100\ R = \frac{100\ (Po - P)}{\underline{M}\ Po} \quad \text{where}$$

Po = V.P. H_2O; $\underline{M}$ = moles/1000 g. H_2O; P = V.P. of solution. For Potassium Hydroxide, at 25°, when $\underline{M}$ = 10, 100 R = 5.62.

$$\text{Hence} \quad P = Po - \frac{100R \cdot Po^{M}}{100} = 24 - \frac{5.62 \cdot 24.10}{100} = 10.5 \text{ mm.}$$

This vapor pressure correction is valid only when the gas is measured over pure 10 M potassium hydroxide. This obviously was not done since some potassium carbonate would be formed by absorption of the carbon dioxide used to sweep out the apparatus. However, since the vapor pressure values in I.C.T. for potassium carbonate solutions closely parallel those for potassium hydroxide it was assumed that the error would be negligible if fresh 10 M potassium hydroxide was used for each run.

Validity of the above method of measurement was checked by transferring several gas samples measured over potassium hydroxide to a water burette and again measuring the volume.

The results were as follows:

	Over Water	Calculated by v.p. change
I. 30 ml. of air over 36 per cent KOH	30.5 ml.	30.52
II. 50 ml. of air over 36 per cent KOH	50.8 ml.	50.87

It was thereby concluded that at 25° a vapor pressure correction of 10.5 mm. is correct and this value was used for calculating results tabulated below.

	Vol. Collected	Vol. at 0° 760 mm.	Capacity by volume	Capacity on Wt. Basis
Run I.	Parent Compound, V-8.		743 mm.	24°
	32.8 ml.	29.1	4.58	4.60 per cent
Run II.	Parent Compound, V-8.		743 mm.	24°
	34.3	30.4	4.81	4.68 per cent
Run III.	Di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt Preparation L-33A		743 mm.	24°
	55.1	49.0	3.98	4.06
Run IV.	Di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt Preparation L-33A		743 mm.	24°
	57.9	51.4	4.17	4.21
Run V.	Di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt Preparation L-33A		743 mm.	24°
	61.7	54.6	4.43	4.39

Run VI. Di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt
Preparation L-33A 743 mm. 24°

Vol. Collected	Vol. at 0° 760 mm.	Capacity by volume	Capacity on Wt. Basis
58.5	51.9	4.21	4.37

Run.VII. Compound of Henselmeier III, 2: 6.4 per cent,
744 mm. 24°

9.6 ml.	8.7 ml.	4.14	4.84[1]

Run VIII. Compound of Henselmeier IV, 2-1, 5.5 per cent,[2]
744 mm. 24°

25.0	22.0 ml.	4.10	5.5

Notes on above:

1. This capacity is based on loss in weight upon deoxygenation by carbon dioxide. Value reported by Henselmeier was 6.4 per cent. The capacity on a weight basis by reoxygenation was 4.34 per cent.

2. This capacity was the value reported by Henselmeier.

It may be concluded from the above that this compound probably may be made to absorb oxygen to a value a few tenths of a per cent above its theoretical capacity, but it is thought that values of several per cent above the 4.15 value are probably due to the gradual accumulation of moisture and to weighing errors which became relatively large when small samples were used.

(5) Synthesis of Di-(2-hydroxy-3-methoxybenzal)ethylenediimine Cobalt.

(a) The Pyridine Method. The compound di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt was prepared by a procedure proposed by Calvin for the preparation of the parent compound (see his Report OEM-sr 403, Serial Number 186, p.2). By this procedure the cobalt salt is dissolved in a solution of ethylenediamine, pyridine and water. The aldehyde is then added, and the mixture heated to 80°. The air is evacuated from the reaction flask during the preparation of the compound. The material is finally centrifuged and dried at 100° under a vacuum. By this procedure, the parent compound is obtained as a monopyridinate, which, in the hands of Calvin, can be activated by the removal of the pyridine at 170° under a vacuum.

This procedure was applied to the preparation of di-(2-hydroxy-3-methoxybenzal)ethylenediimino cobalt. A material was obtained having an oxygen capacity of only 2.7 per cent. The preparation of Co-Ox M by this method was found to be entirely unsatisfactory and this has been since confirmed by Calvin.

(b) <u>The Original Alcohol-Water Method</u>. This method of preparation involves the mixing of ethylenediamine, cobalt salt, and aldehyde in a 50 to 60 per cent alcohol medium. This method gave excellent results in the preparation of Co-Ox M, the compound being obtained in the form of golden, needle-shaped crystals. Upon activation at 165° under a vacuum the compound changed from golden yellow to maroon, and carried the theoretical capacity of 4.1 per cent oxygen. The yields by this method were about 60 per cent. It is believed that for laboratory preparations of Co-Ox M this method yields a pure product which is easily filtered and more easily handled in subsequent operations than the material obtained by any other method.

(c) <u>The Direct Mixing Method Using a Suspension of the Condensation Product in Water and the Cobalt Salt</u>. By this method of preparation a suspension in water of the finely pulverized Schiff's base is digested for several hours with a solution of the cobalt salt. The compound obtained is filtered or centrifuged, dried and activated in the usual manner. The oxygen capacity of the final product obtained closely approached its theoretical value providing that the period of digestion had been long enough to insure complete reaction. Usually twelve hours or more on a steam bath are required. In general this method of preparation was not as satisfactory for the preparation of Co-O. M as other methods. However, for the preparation of some compounds, e.g. the 3-nitro compound, this is the only satisfactory method that has been devised.

(d) <u>The Direct Mixing in Water of the Cobalt Salt Diamine and Aldehyde</u>. Co-Ox M has been prepared in a satisfactory manner by the direct mixing of a cobalt salt, ethylenediamine and aldehyde in water solution, only enough alcohol being employed to dissolve the aldehyde. With ample stirring and with a sufficient digestion period at about 80° a satisfactory product was obtained. The reaction mixture was buffered with acetic acid and sodium acetate when cobalt chloride was used. By this method a yield of 90 per cent was obtained. The compound was readily activated in the usual manner and a product of 4 per cent capacity was consistently obtained. One difficulty with this method lies in the fact that the material was very difficult to filter especially after washing with water following the first filtration. Additions of alcohol to the wash liquid did not eliminate this difficulty. Several hours digestion of the steam bath with the wash liquid improved the filtering characteristics to a small extent. Another objection to this method was the formation of some Schiff's base which did not entirely react with the cobalt salt since small amounts of yellow oil was always produced upon activation. This difficulty might not be encountered if sufficient digestion were employed.

(e) Preparation of Co-Ox M from the Sodium Salt of the Condensation Product without the Preliminary Isolation of the Condensation Product. Co-Ox M has also been prepared by dissolving the aldehyde in a hot water solution of sodium hydroxide followed by the addition of solutions of cobalt salt and ethylenediamine. This method yielded a material which was extremely difficult to filter; upon activation in the usual manner the product showed nearly theoretical oxygen capacity. Although this method is considered inferior to several of the other suggested methods it is of interest that a satisfactory active product is obtained inasmuch as the parent compound cannot be prepared in active form by this method.

(f) Preparation in Dilute Alcohol Medium from the Sodium Salt of the Condensation Product. One of the best methods that was devised for preparing Co-Ox M involves the preparation of the Schiff's base in about 50 per cent alcohol, followed by the formation of its soluble sodium salt by the addition of hot, caustic solution and finally the precipitation of the cobalt derivative by the addition of a solution of the cobalt salt buffered with acetic acid and sodium acetate. The final concentration of alcohol was thereby about 25 per cent.

Several attempts were made to eliminate all or most of the alcohol by precipitating the Schiff's base from a very dilute solution of ethylenediamine in water. It was found however that large particle size of the Schiff's base formed in this manner was difficult to dissolve in the hot caustic solution. When the Schiff's base was precipitated as suggested above the particle size of the material was such that it dissolved immediately upon the addition of the hot caustic solution. The minimum alcohol concentration for this step in the procedure was found to be about 50 per cent. This was obtained by adding an alcohol solution of the aldehyde to a hot solution of ethylenediamine dissolved in water. By this method a product was obtained that was readily filtered and no appreciable difficulty was experienced in filtering the material after reslurrying with warm water. Occassionally however, it was found necessary to add a small amount of alcohol to the wash solution in order to minimize colloid formation which rendered the final filtration difficult.

The yields by this method of preparation were from 85-90 per cent. Upon activation in the usual manner, compounds prepared in the above described manner carried 4.1 per cent.

This procedure was the basis for the large scale preparations described in this report under subsection (7).

(g) Survey of the Above Methods. It is of interest that Co-Ox M can be prepared by such a wide variety of methods, and that the conditions may vary within rather wide limits and a satisfactory product obtained. However not all of the methods just described above are of equal merit. The pyridine method of Calvin ((a) above) the least satisfactory of the methods investigated since the compound prepared by this method was of very low capacity, and the procedure was less easily carried out.

The method employing a suspension of the Schiff's base in water ((c) above) was not considered to be entirely satisfactory since a long period of digestion with agitation was found necessary to obtain a good product.

The alcohol method employing an alcohol concentration of 50-60 per cent ((b) above) was considered to be unsatisfactory for large scale preparations inasmuch as the yields were only 60 per cent and the large amount of alcohol required was not economical.

The other two methods described in which no alcohol was used ((d) and (e) above) were not considered entirely satisfactory since filtration was extremely difficult and the final product was slightly contaminated with unreacted Schiff's base.

The method described in part (f) of this section was considered to be the most satisfactory for moderate scale preparations since the final product was easy to filter, of high purity, and was obtained in good yield. None of the other methods are entirely adequate in all of these respects.

For further details in regard to the studies that have been made on the various methods of preparation consult Report XXVII, Section III, and Report XXXVIII, Section III.

(h) The Activation of Di-(2-hydroxy-3-methoxybenzal)ethylenediimine Cobalt in High Boiling Solvents. The method generally employed to convert the hydrated Co-Ox M into the active oxygen carrier consists in heating the material to 170° under a vacuum. This method, while conveniently carried out on a small sample in the laboratory, became a difficult task when large scale preparations were undertaken. It was thought possible to remove the water of hydration by heating a suspension of Co-Ox M in an inert liquid having a boiling point of 170°, or above the usual activation temperature of the material. Several experiments were conducted using high boiling solvents among which were butyl cellosolve, p-cymene, and mineral oil.

Upon heating in butyl cellosolve to 170° the material turned from tan to a very dark reddish-brown. However after filtering the material and drying at 100° in a vacuum the compound returned to its original yellow color and showed no oxygen capacity. Upon heating in a vacuum at 170° it became active, changing to reddish-brown in color and absorbed 3.8 per cent oxygen.

The compound obtained after heating in p-cymene was deep purple in color. Even after heating the dried material at 100° for several hours in a vacuum the odor of p-cymene was perceptible, but no color change was noticed, and the material did not carry oxygen. Heating at 170° produced no visible change, and the capacity was only 0.9 per cent.

Using mineral oil as the heating medium similar results were obtained. Although one sample was heated to 200° without apparent decomposition; no activation resulted.

For further details of the technique employed in these studies consult Report XXXVIII, Section X, and Report XLV, Section VIII.

(6) Large Scale Preparation of Di-(2-hydroxy-3-methoxybenzal)-ethylenediimine Cobalt. Following the laboratory work on the preparation of Co-Ox H by different methods, as described in subsection (5) above, the size of the batches was gradually increased and the procedure further modified for application to batches of about 15 pounds. The equipment and method used is described below. A more complete description of the work may be found in Report XXXVIII, Section IV.

(a) Equipment. These preparations were carried out in 20 gallon stoneware crocks, set on dollies so that they could be moved around as desired. The various solutions were heated by means of 70 pound steam passing through copper coils which could be immersed in the liquids. In general the water was heated before the addition of any chemicals. The solutions were stirred by hand using wood paddles. Solid materials were filtered on large Buchner funnels. These funnels were constructed by cutting a 55 gallon steel alcohol barrel into thirds and welding pipe nipples into the center of the end pieces. These funnels were carried on dollies and were connected by unions to 30 gallon tanks which were connected to a large vacuum pump and acted as receivers for the filtrate. The filter used in these funnels consisted of cloth laid over two or three layers of coarse screen, which allowed passage of the liquid to the outlet in the center. The crocks were wheeled up a ramp to a platform directly above the funnels when it was desired to transfer material to the funnels.

After filtration, the product was dried in the drying cabinet shown in Figure 1 of the accompanying drawing which contained banks of heating lamps at the top and bottom and supports for five wire trays. By means of fans, air was circulated past the heating lamps, over the compound and out the holes in the side. The total heat which could be supplied to the cabinet by the heating lamps was approximately 8000 watts. This was, in most cases, too much heat and the banks of lights were adjusted so that the top one gave about 1000 watts while the lower one gave about 3000. This amount of heat was sufficient to keep the temperature at about 80° during the period while the compound was still quite wet and to raise the temperture to the maximum of about 110° as the compound became dry. This drier very satisfactorily dried a 30 pound batch of compound in about 24 hours.

The dried compound was ground in a small burr mill powered by a 0.25 h.p. motor. It was found that the material could be ground only if it was dried very thoroughly. However, in several cases where attempts were made to grind insufficiently dried compound and the mill was clogged, it was found possible to finish the grinding by adding some thoroughly dried, previously ground material to the material in the grinder. With properly dried material, this mill would grind an 8 pound batch in 5-10 minutes.

Several different methods of activating the compound were tried. The first activator, Fig. 2, consisted of a trough about 6 ft. long in which a four-bladed paddle wheel turned at about 10 r.p.m. The heat in this activator was supplied by heating lamps suspended over the trough. Some compound was satisfactorily activated in this piece of equipment, but it was found that the temperature was so difficult to control that rather frequently part of the compound in a batch decomposed or burned.

The second activator, Fig. 3 consisted of an 18 gallon tank with a flanged end which rotated in an oil bath which was kept at 170-190°. This rotating drum was fitted with packing glands so that carbon dioxide could be passed through the material during the activation. Fins were welded into the drum and several loose fins were added to mix the material and knock loose any material which might cling to the walls of the drum. This piece of equipment worked fairly well but required constant attention.

A third activator, Fig. 4, was built which employed the rotating drum from the oil bath activator. The heating unit in this activator was electrical and the rotating drum and heating units were insulated by means of a good, double walled, insulated transite box. This activator had a capacity of about 25 pounds per day, although it required attention every 12-15 hours. An excellent activator should also be equipped with packing glands

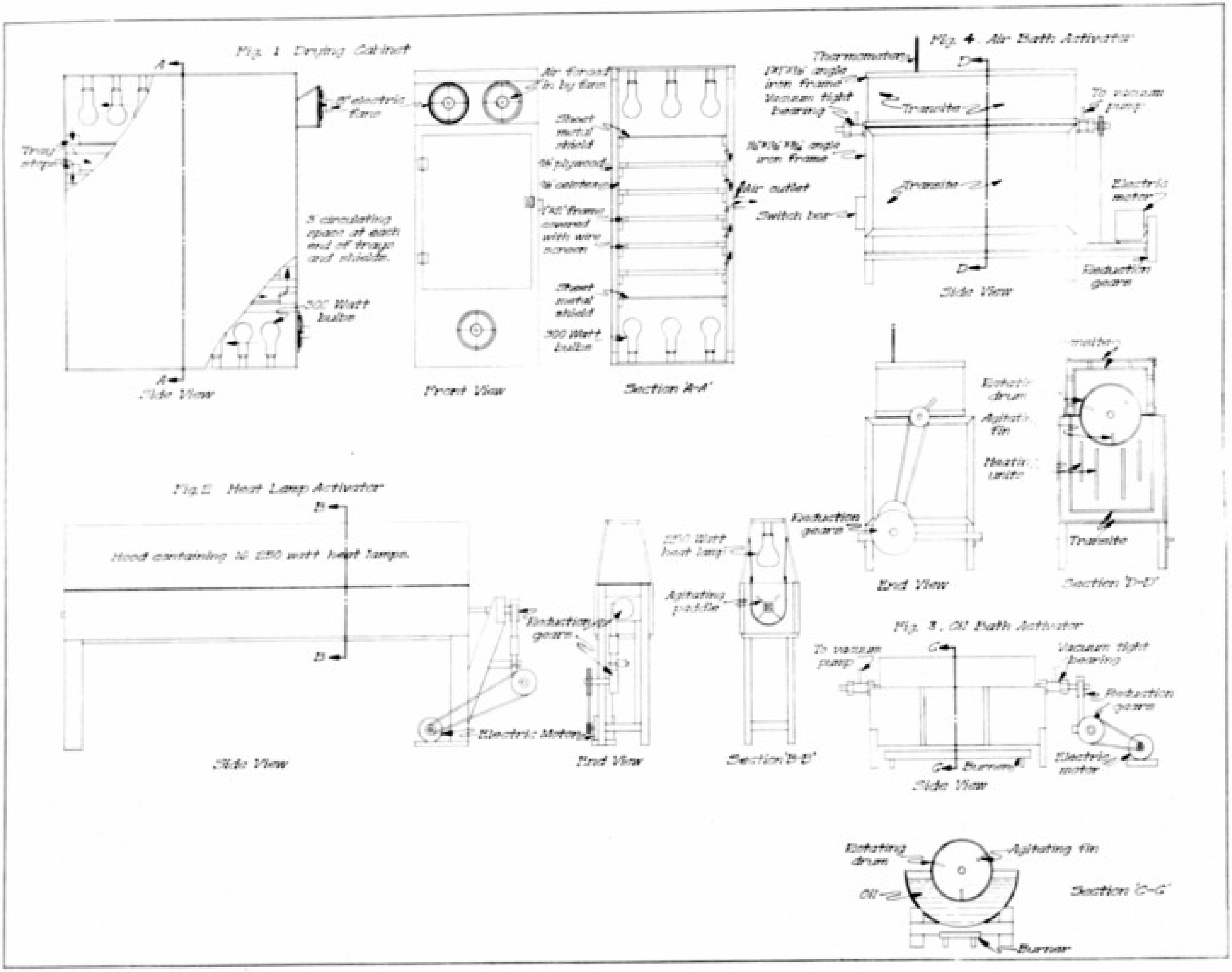


Fig. 1 Drying Cabinet
Tray stops
8" electric fans
3 circulating spaces at each end of trays and shields
300 Watt bulbs
Side View
Front View
Air forced in by fan
Sheet metal shield
1/4" plywood
1/4" celotex
Frame covered with wire screen
Sheet metal shield
300 Watt bulbs
Air outlet
Switch box
Section A-A'
Fig. 4. Air Bath Activator
Thermometer
Angle iron frame
Vacuum tight bearing
Transite
Angle iron frame
Transite
To vacuum pump
Electric motor
Reduction gears
Side View
End View
Rotating drum
Agitating fin
Heating units
Transite
Section D-D'
Fig. 2 Heat Lamp Activator
Hood containing 16 250 watt heat lamps.
Reduction gears
Electric Motor
Side View
End View
250 Watt heat lamp
Agitating paddle
Reduction gears
Section B-B'
Fig. 3. Oil Bath Activator
To vacuum pump
Vacuum tight bearing
Reduction gears
Burner
Electric motor
Side View
Rotating drum
Agitating fin
Oil
Burner
Section C-C'

and filter which would enable the passage of dry carbon dioxide at the rate of at least 0.5 cu.ft. per minute. The optimum temperature of this type of activator appeared to be 180°.

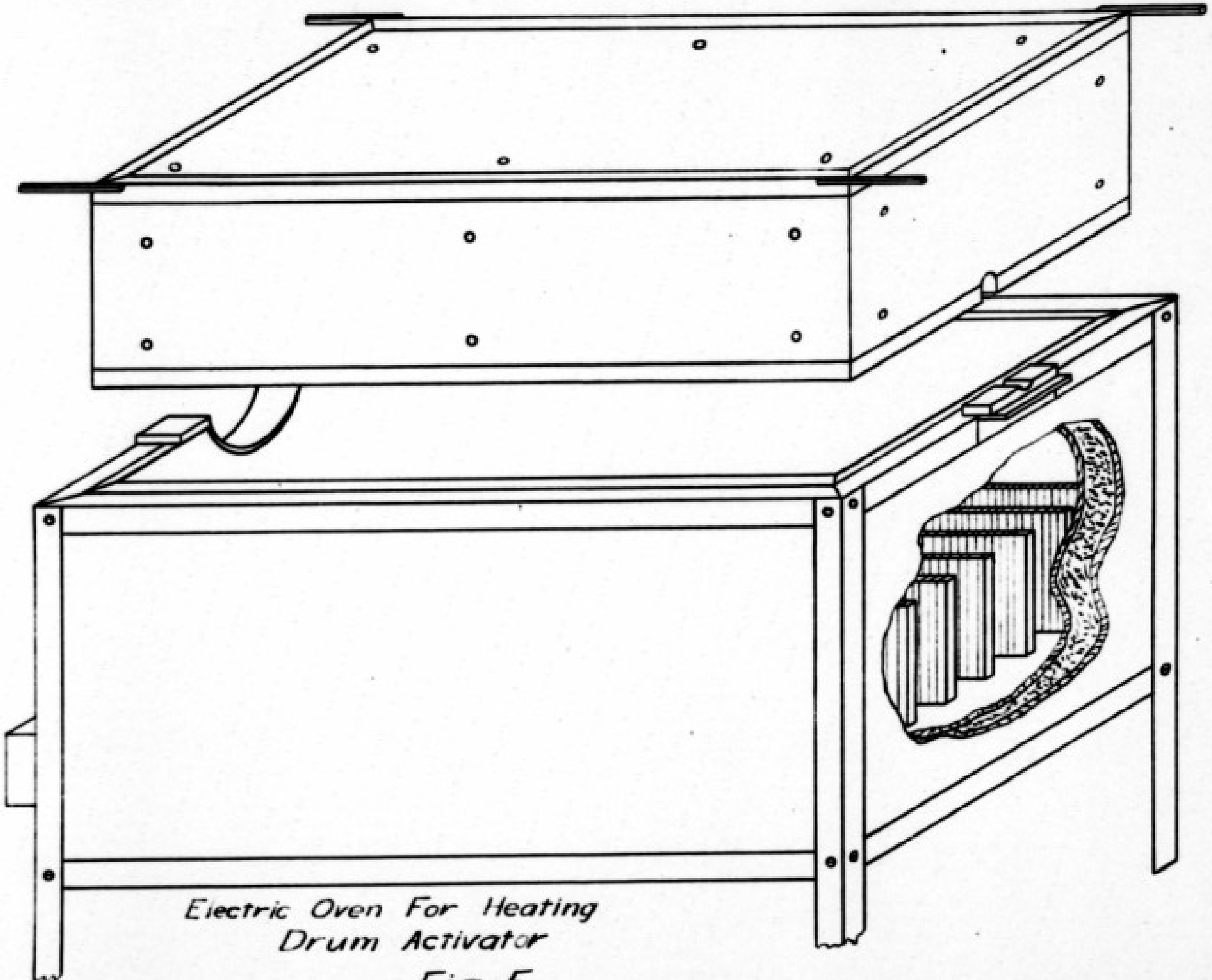
The cost of the above activator was quite high since a great deal of carbon dioxide was consumed. The carbon dioxide was generated from dry ice for this apparatus. It was found that when a stream of gas was continually passed through the activator tank, the filter on the discharge end became clogged, and a proper flow of gas was difficult to maintain. Since the carbon dioxide generators did not develop much pressure, a satisfactory carbon dioxide flow was not maintained.

The apparatus was then modified so that nitrogen could be recirculated, first through the activator tank and then through a tank of walnut caustic potash. This system was found unsatisfactory also because the filter in the discharge end of the activator tank became plugged and prevented an adequate gas flow.

The apparatus was the modified (Fig. 5) so that a tank of caustic potash was attached to the activator tank by means of a five inch pipe and stuffing box. This system worked quite well, though it required considerable attention to keep the large stuffing box properly lubricated. The stuffing box often stuck because the grease worked out.

Since the dependability of the apparatus was so very poor, it was decided to allow the activator tank to remain stationary and to fill the activator tank completely with compound and to allow the heating to take place only by natural conduction. The time of activation of a batch was thereby lengthened to about 3 days, although 50 pounds of compound could be activated at a time, and no attention was required. This latter system seemed to be the best system yet devised since it was much easier to maintain a high vacuum with the stationary system since no trouble was encountered with the stuffing box. Also only light filters were required on the activator and caustic potash tanks. This allowed the vapor flow to take place much more freely.

In another experiment the compound was placed in a container together with a drying agent. The container was then placed in an oven at 115°. The activation proceeded slowly. Of the various drying agents tried, only barium oxide and phosphorous pentoxide were capable of activating the compound at 115°. The activation was complete in about 24 hours. A plywood box was built and filled with the compound. Cloth bags of barium oxide were buried in the compound, the box was sealed and then placed in an oven at 115°, the intention being to leave the compound in the oven for a period of a week or more. However, the heat of hydration of the barium oxide was so great that the cloth bags containing it were charred and the compound was ignited. Although



Electric Oven For Heating
Drum Activator

Fig. 5

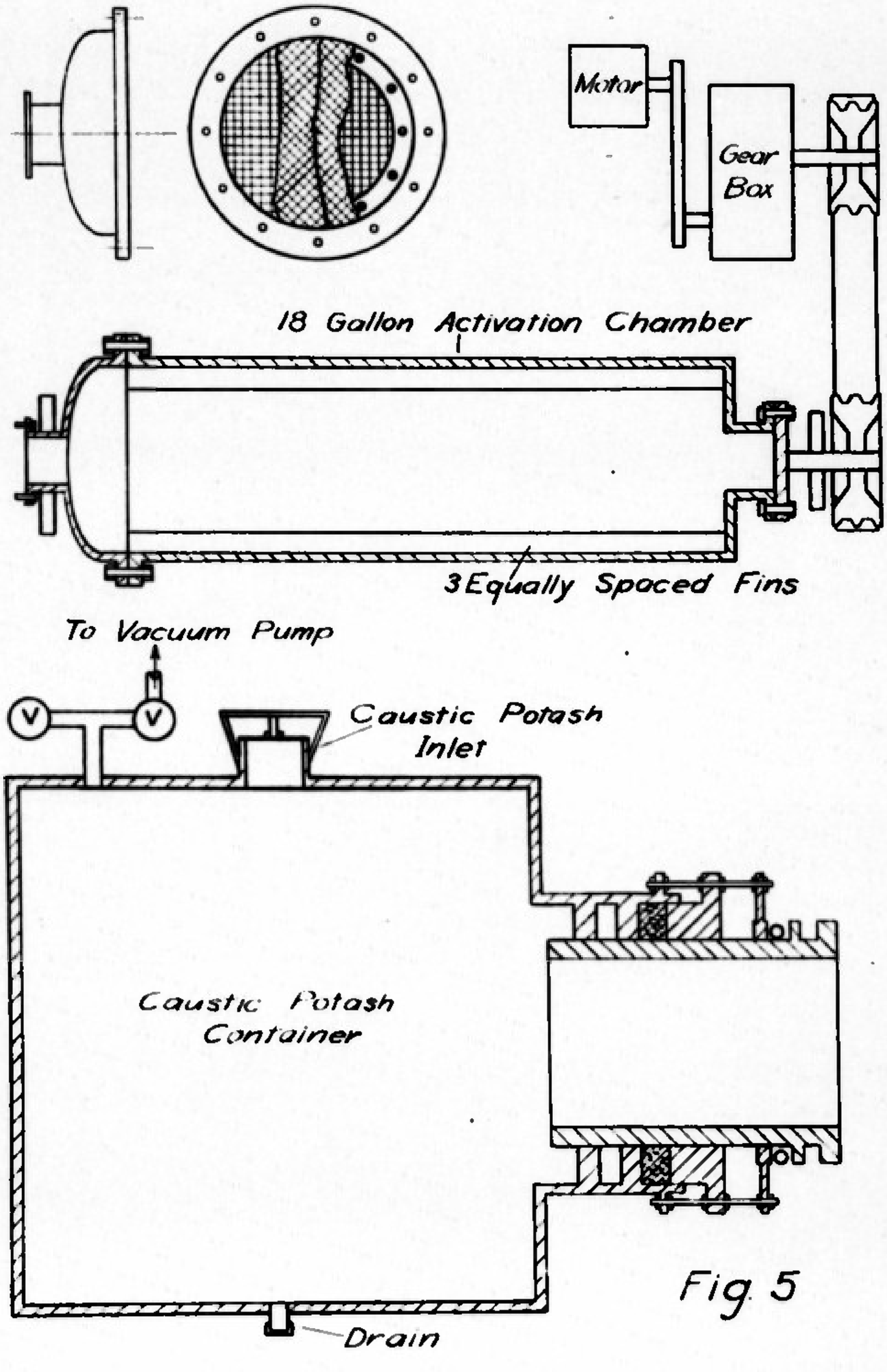

Motor
Gear Box
18 Gallon Activation Chamber
3 Equally Spaced Fins
To Vacuum Pump
V
V
Caustic Potash Inlet
Caustic Potash Container
Drain

Fig. 5

this proved unsatisfactory, the principle is sound and if the barium oxide were placed in the containers in such a way that the heat of hydration could be removed, the process would undoubtedly be satisfactory.

(b) Method of Preparation. The method of preparation described previously in subsection (5), article (f) above was employed in this work and some 16 preparations totaling over 150 pounds of material were made. Various modifications of this procedure were employed on some of the large scale preparations in an effort to make the procedure more economical. It was found that the amount of alcohol could be reduced considerably below the 25 per cent concentration which was used in the first preparations. When the final alcohol concentration was reduced below 15 per cent the material was very difficult to filter. The volume of water used to dissolve the sodium acetate used for a buffer was decreased to a minimum and also the water used to dissolve the diamine and the cobalt salt. These reductions in the amount of water used made possible the elimination of even more alcohol without decreasing the final alcohol concentration below 15-20 per cent. As a result of these modifications the amount of alcohol was reduced to about one half of that originally employed, and the weight of compound produced per unit volume of solvent was considerably increased. All of these modifications were made without changing the quality of the final product.

On the basis of these large scale studies a procedure was devised which is considered superior for large scale work. This recommended procedure will be given in detail below.

(c) Recommended Procedure for the Preparation of Di-(2-hydroxy-3-methoxybenzal)ethylenediimine Cobalt (Co-Ox M). In a 20 gallon crock heat 16 l. of water to boiling and dissolve in it 0.95 l. of 68.5 per cent ethylenediamine. In another crock heat 8 l. of alcohol to boiling and dissolve in it 2.66 l. of 2-hydroxy-3-methoxybenzaldehyde. Add this hot solution of the aldehyde to the diamine solution and stir thoroughly. In another crock heat 4 l. of water to boiling and dissolve in it 0.82 kg. of sodium hydroxide and 0.41 kg. of sodium acetate. Add this solution to the crock of condensation product and stir thoroughly until all the crystalline material has dissolved. In another crock heat 8 l. of water and 0.4 l. of acetic acid to boiling and dissolve in them 2.5 kg. of cobalt chloride. Add this hot cobalt solution to the solution of the sodium salt of the condensation product, and stir vigorously for 15 minutes. Then allow the material to stand at least one hour before filtering. Return the filtered material to the original crock and mix thoroughly with 40 l. of water. Filter, and repeat the washing process. Filter the material as dry as possible on the Buchner funnel, and place in a drying oven such as described in article (a) above in which a stream of warm air sweeps over the compound.

Carry out the final drying at a temperature of 110°. After the material is completely dry throughout the mass, grind the chunks in a burr mill. Activate the material in a vacuum at a temperature of 170-180°.

(7) Rate of Oxygenation of Di-(2-Hydroxy-3-methoxybenzal)-ethylenediimine Cobalt at Various Temperatures. The gravimetric method described in detail in Section X, part C, subsection (1) of this report was used to determine the rate of oxygenation of Co-Ox M at several temperatures. The results of this study, covering a range of temperatures from 25° to -70°, are shown in the accompanying graph. The conclusions reached in this work may be summarized as follows:

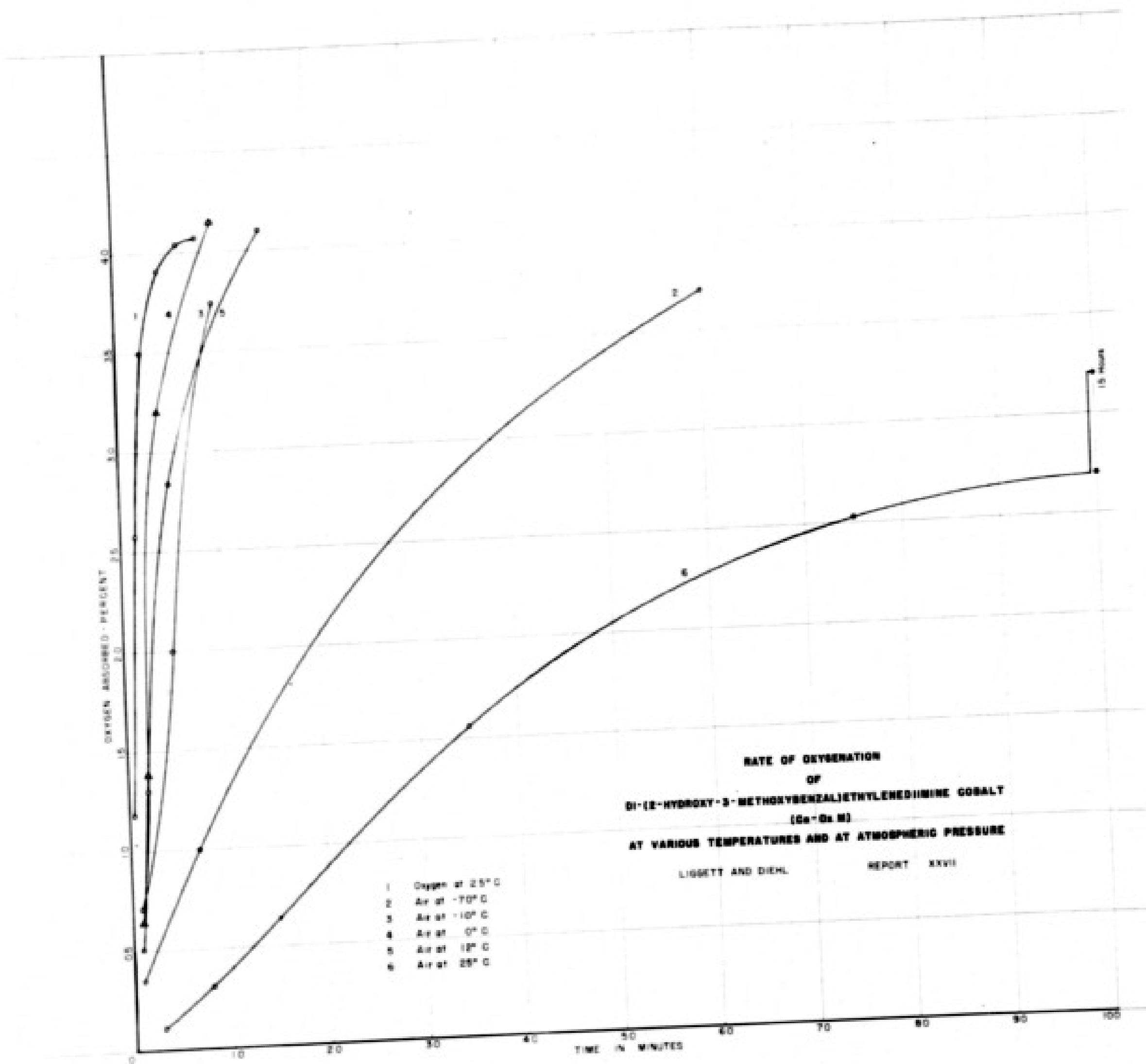
1. The compound is oxygenated very slowly by air at 25°, about fifteen hours being required for saturation, and it is doubtful if the theoretical capacity is actually reached under atmospheric pressure at this temperature. With pure oxygen at this temperature saturation of the compound is attained in eight minutes.

2. The rate of oxygenation using dry air increases remarkably at temperatures somewhat below 25°. At 0° saturation was reached in about ten minutes. This compares favorably with the rate obtained when pure oxygen was used at room temperature. At a temperature of -70°, obtained by employing a chloroform and dry ice bath, the rate is very much slower than at 0°. In this instance, even at this extremely low temperature, it is interesting that the rate is still somewhat more rapid than at room temperature.

3. Rates made at + 12° and at - 10°, indicate that the optimum rate occurs within this range.

4. By comparisons with the rates on the parent compound previously reported by Hoch, this compound was found to be very much more rapid especially at temperatures below 12°. As compared with the 3-nitro compound the rate of this compound is slower, but it has an advantage over the 3-nitro compound in that it may be deoxygenated at a lower temperature. Other experiments have indicated that this compound may be completely deoxygenated at 55° under atmospheric pressure. It is probable that it may be completely deoxygenated by a vacuum at a considerably lower temperature.

In addition to the rates determined by the gravimetric method as described above, two other methods were employed. The rate of oxygenation in pure oxygen was determined using the differential manometric apparatus described in this report, Section X, Part A. The rate in air was also determined using


RATE OF OXYGENATION
OF
DI-(2-HYDROXY-3-METHOXYBENZAL)ETHYLENEDIIMINE COBALT
(Co-Ox M)
AT VARIOUS TEMPERATURES AND AT ATMOSPHERIC PRESSURE
LIGGETT AND DIEHL
REPORT XXVII
1 Oxygen at 25° C
2 Air at -70° C
3 Air at -10° C
4 Air at 0° C
5 Air at 12° C
6 Air at 25° C
OXYGEN ABSORBED - PERCENT
TIME IN MINUTES
15 Hours

the manometric rate apparatus described in this report, Section X, Part C, subsection 2. The results from both of these apparatus are in accord with those just described. A comparison of the rates of oxygenation of the methoxy compound with other compounds will be found in Section X, Part C.

(8) Studies on the Absorption of Moisture by Di-(2-hydroxy-3-methoxybenzal)ethylenediimine Cobalt and Its Effect on its Oxygen Carrying Capacity. As implied in subsection (4) above the erroneous, high capacities first reported for di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt were due to the absorption of water by the material. Early experiments with the machine described in Section XI of this report indicated that the material was markedly hygroscopic and that this would play an important part in the use of the compound. It therefore became of interest to examine the behavior of the material toward water.

Weighed samples of both the oxygenated and the deoxygenated forms of the compound were placed in a humidifier which allowed them access to air saturated with water vapor at 30°. It was found that the oxygenated sample, containing its theoretical oxygen capacity, when so exposed increased in weight from 15-20 per cent of the weight of the sample taken in periods ranging from 10-24 hours. Upon being dried at exactly 100° under a vacuum, it retained 2.3 per cent of this moisture, and could then be re-oxygenated, the theoretical amount of oxygen again being absorbed. The moisture which was retained at 100° under a vacuum was lost upon heating to 170° without noticeable decrease in the oxygen capacity after this treatment.

In the case of the deoxygenated samples an entirely different effect was observed. A deoxygenated sample, previously having been shown to carry theoretical capacity, upon exposure to air saturated with water vapor increased in weight up to 15 per cent and upon oxygenation in pure oxygen at 175 pounds pressure carried but 1.9 per cent or a decrease of 2.3 per cent from its original value. When this material was heated at 100° in a vacuum, nearly 2 per cent of the moisture was retained and the capacity of the material was only 2.9 per cent. This material could only be completely reactivated by heating to 170° in a vacuum.

There was no appreciable change in color observed upon exposing the deoxygenated sample to air saturated with water vapor. It seemed probable that under such conditions the compound absorbed moisture in preference to oxygen.

From the above it may be concluded that when the deoxygenated form of the compound has been exposed to moisture it becomes inactive, and can only be restored by complete reactivation. The reversible capacity based on the deoxygenation at 100° would be 2.9 per cent.

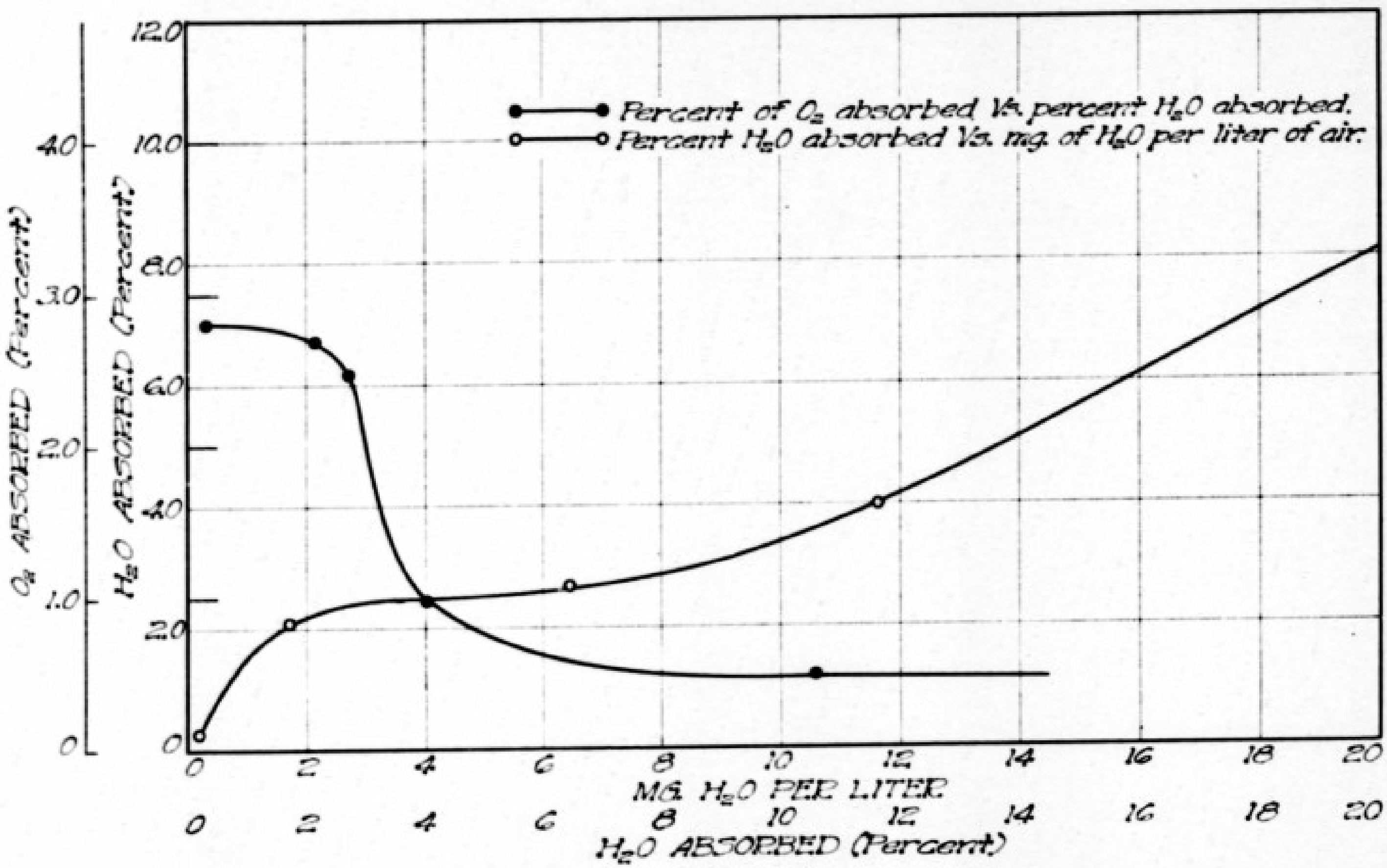
Since there was no change in color upon absorption of moisture by the deoxygenated compound, it might be concluded that there was no actual chemical reaction involved in which the material changed to its original yellow inactive form. However, several instances were observed whereupon a deoxygenated sample which had been exposed to moist air changed to a yellow color identical with the original unactivated material. This phenomena was observed upon heating the moist sample somewhat above room temperature. It would therefore seem very probable that there is a definite chemical reaction in which the material is actually deactivated by reaction with the moisture and occurs at a temperature between 60 and 100°.

In order to obtain information relative to the rate of hydration as compared to the rate of oxygenation, samples of active, deoxygenated di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt were exposed to air of various humidities and the amount of oxygen and moisture absorbed under these conditions determined. The compound used (L-39) had a capacity of 4.1 per cent. The samples of about 2 g. were weighed into identical nickel boats, deoxygenated at 170° under a vacuum for 15 minutes, cooled in an evacuated desiccator, then quickly weighed and placed inthe humidifiers.

The humidifiers were made from desiccators of the same size. The moisture content in the air of the humidifiers was controlled by means of sulfuric acid solutions of the proper concentrations. The acid concentrations were determined by specific gravity determinations using a pyknometer, and the moisture content of these solutions was calculated in mg. of water per liter, from the vapor pressure data for sulfuric acid solutions taken from International Critical Tables, Vol. III, p. 303.

The five samples were placed in the humidifiers for a period of 60 hours. The total gain in weight which is the water and oxygen absorbed at the end of this period, was measured. The gain in weight due to absorption of water alone was measured by placing the sample in an electrically heated tube at 170° and passing dry nitrogen over the sample at this temperature and collecting the moisture in a weighed U tube filled with magnesium perchlorate.

The data is summarized in the accompanying graph from which it is evident that the percentage of oxygen absorbed decreased markedly with water absorbed.



Percent of O_2 absorbed Vs. percent H_2O absorbed.
Percent H_2O absorbed Vs. mg. of H_2O per liter of air.
O_2 ABSORBED (Percent)
H_2O ABSORBED (Percent)
MG. H_2O PER LITER
H_2O ABSORBED (Percent)
0
1.0
2.0
3.0
4.0
0
2.0
4.0
6.0
8.0
10.0
12.0
0 2 4 6 8 10 12 14 16 18 20
0 2 4 6 8 10 12 14 16 18 20

An experiment was designed to conclusively show that the active Co-Ox M can be made to react with moisture and that the original hydrated form will result. In this experiment an active sample of Co-Ox M having a capacity of 4.1 per cent, digested in water on a steam plate for 12 hours. The color of the material changed from a reddish-brown to the familiar yellow color of the hydrate. After drying in a vacuum at 100° for 12 hours the material was activated by heating the material to 170°. The loss in weight upon activation was 4.65 per cent which checks with the value reported by Calvin and values found by the activation of the original hydrate. The capacity of this material remained unchanged from that of the original material. From these experiments it was concluded that the air employed for the oxygenation of Co-Ox M must be thoroughly dried to a value at least below 0.2 mg. of water per liter of air.

For the details of the above experiments, see Report XXXVIII, Section V.

(9) <u>Magnetic Susceptibility of Di-(2-hydroxy-3-methoxybenzal)-ethylenediimine Cobalt. By Calvin at the University of California.</u> Measurements of the magnetic susceptibility of di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt were made at California. The inactive material as first prepared, two samples, (a) and (b), of the activated material, and the activated and oxygenated material were measured. Active sample (a) was prepared by activating the material in a vacuum drying pistol and filling the magnetic tube with active sample; the oxygen was pumped off at 100° using an aspirator. On removing the tube after measurement, the sample was not active. Three layers were found in the tube, the top one of which was very similar in appearance to the inactive material, the middle one was brown, resembling the active form not previously observed. Active sample (b) was activated in the magnetic tube by heating at 170° and pumping by a Nelson pump. The data seems to indicate that the active sample picks up water rapidly and becomes inactive (see Report XXXVIII, Section V).

$$T = 295°$$

Hydrate	Xm	=	8500×10^{-2}	3 electrons
active sample (a)	Xm	=	5400×10^{-6}	- - - - -
active sample (b)	Xm	=	2500×10^{-6}	1 electron
peroxide (1/2 O_2)	Xm	=	weakly paramagnetic	

The magnetic susceptibility of sample 3 (Liggett L-12D) Section VI, Report XXXVIII, was also measured.

$$Xm = 5100 \times 10^{-6}$$

The procedure of measurement was the same as that employed in measuring active sample (a). After measurement the activity was tested and found to be less than 1 per cent. The magnetic data indicate a mixture of 1 and 3 electron forms, possibly hydrate and active form. The low activity agrees with this.

Further details of these measurements are given in Report XXXVIII, Section VI.

(10) The Pressure of Oxygen Above Di-(2-hydroxy-3-methoxybenzal)-ethylenediimine Cobalt. By Calvin at the University of California. The oxygen pressure above di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt was determined using the apparatus described earlier in connection with similar measurements on the parent compound. The determinations were run at 25° and the equilibrium was approached from above.

Oxygen Pressure in mm. Hg	Extent of Oxygenation in per cent
36	20.1
56	39.9
76	67.6
99	79.6
403	97.0

Similar data on the parent compound and on di-(3-nitrosalicylal)-ethylenediimine cobalt (Calvin Monthly Report, May 15, 1942) have been reported.

(11) The Rate of Deterioration of Di-(2-hydroxy-3-methoxybenzal)-ethylenediimine Cobalt. Two determinations of the rate at which Co-Ox M deteriorates were determined. The first determination was made in the machine built by Gilliland (first sent to McLean at Chicago for toxicological studies) for making life tests of the compound and was put through 2700 cycles. The compound in this machine was contained in a tube 0.5 in. in diameter and about 30 in. in length. This tube held approximately 40 g. of the powdered material. The temperature of the cooling water varied between 10° and 15°. The deoxygenation was carried out with steam at atmospheric pressure. The rate of passage of air was very slow, less than 0.1 cu.ft. per minute. The entering air was at 80 psi, and the exit air was approximately 20 psi. The oxygen was given off at atmospheric pressure. The air used in oxygenation was thoroughly dried being passed through a mechanical trap, a potassium hydroxide drying tower and a magnesium perchlorate drying tower. The cycle was 10 minutes in length, about six minutes for oxygenation and about four minutes for deoxygenation.

The capacity of the material was determined at intervals by removing a portion of the compound from the tube. This sample was heated to 100° in a vacuum to effect complete deoxygenation. The sample after weighing was oxygenated under 200 psi. oxygen pressure for 15 minutes. The compound removed each time was discarded so that any ill effect suffered due to exposure to air would not influence the data.

The rate of deterioration is shown in the following table:

Cycles	Capacity	Rate of Deterioration in per cent of original capacity per 100 cycles
0	4.15	
336	3.71	3.18
1645	2.18	2.82
2700	1.84	0.78

This deterioration is at the average rate of 2.06 per cent of the original capacity per 100 cycles, but as seen from the table the deterioration proceeded much more rapidly at the beginning. This apparent decrease in the rate of deterioration might be due to the fact that the compound was packed in tubes in such a manner, that only the outside layer was fully heated and cooled during the cycle. If such were the case it might be reasonably expected that the outside layer would deteriorate faster and after rather complete deterioration would protect the inner layers in the tube from heat changes to such an extent that the rate of deterioration might seem to slow down.

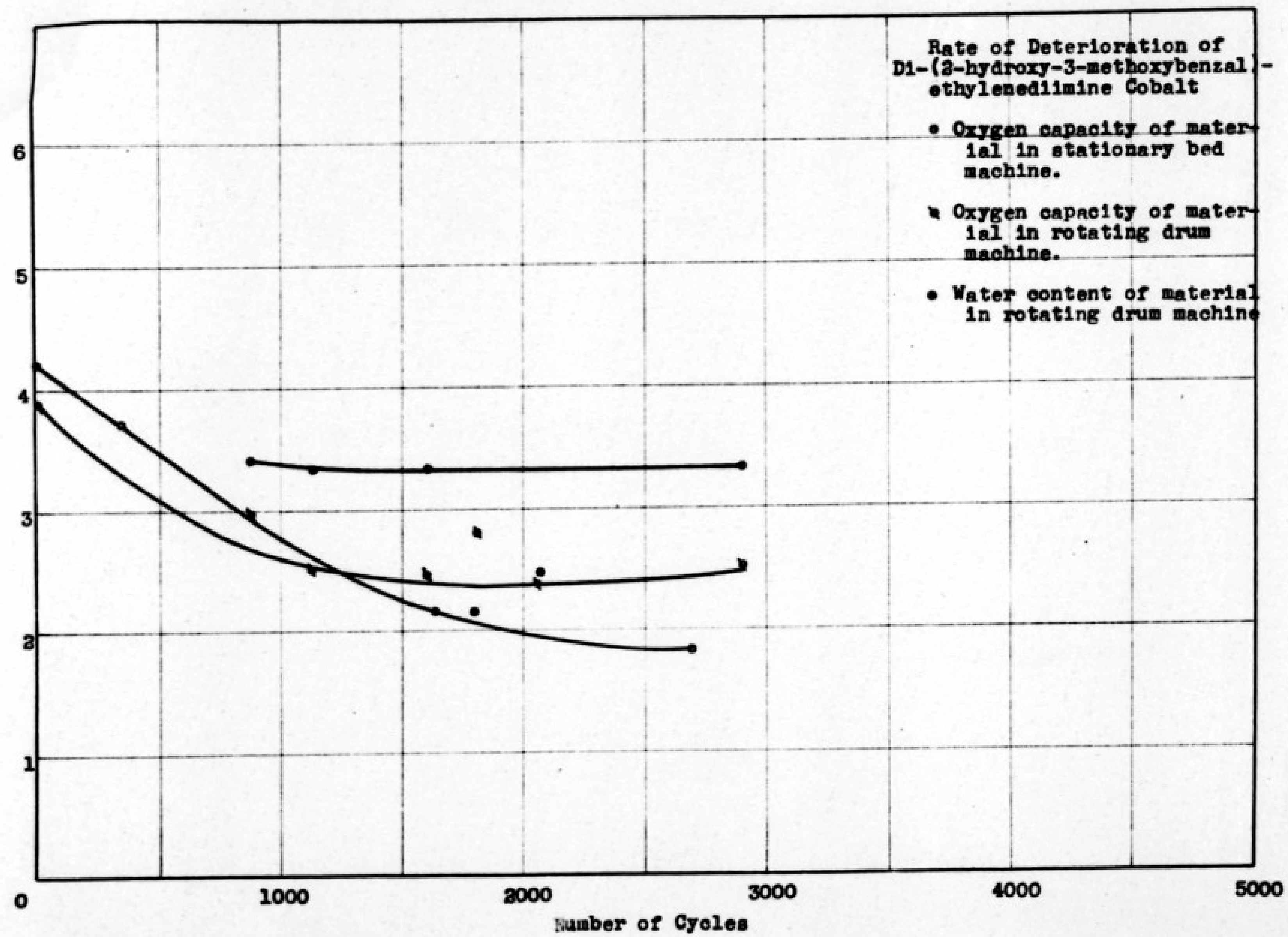
After the final capacity test, the material was heated to 170° in a vacuum. Its capacity was then 2.2 per cent. It appeared therefore that hydration had taken place in some way. The most reasonable source of this moisture, since the air was dried over magnesium perchlorate, is from the combustion of the organic portion of the molecule or possibly exposure of the material when samples were being removed.

The second determination of the rate of deterioration of di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt was determined in the rotating drum machine described in this report, Section X_a, Part B_a. The air used was again dried by passage over walnut potassium hydroxide and magnesium perchlorate. About 8 cu. ft. of air at 80 psig. was passed through the drum during each cycle. Approximately 600 g. of material was contained in the drum so that this amount of air was greatly in excess of that theoretically required. The temperature of the cooling water was 18-20°. The temperature of the steam used was 100°. During the deoxygenation a vacuum was maintained in the drum. While the compound was hot, therefore, it was in a vacuum. This study was begun before the importance of the water absorbed by the compound was fully appreciated and measurements of the water content of the compound were not made until after the test had progressed about 1000 cycles. The amount of water was then determined at the same time the oxygen-carrying capacity was determined. The material contained about 3.25 per cent water, a value which did not change during the period of 1000 to 3000 cycles. The results of this study and of the first study of the rate of deterioration mentioned above are given graphically in the accompanying figure. The rate of deterioration of this material was quite great at the beginning of this experiment but leveled off to a value of 2.4 per cent at about 1500 cycles and did not deteriorate appreciably during the next 1500 cycles. The overall rate of deterioration during the 3000 cycles was 1.3 per cent per 100 cycles.

E. 2-Hydroxy-3-nitrobenzaldehyde (3-Nitrosalicylaldehyde)

(1) The Nitration of Salicylaldehyde. Further work was carried out on the nitration of salicylaldehyde, complementing the work described earlier in which the concentration of the nitric acid used was varied. A series of nitrations were run in which the amount of nitric acid was varied and other factors held constant. The amount of nitric acid was varied from the theoretical amount to a 150 per cent excess; the optimum amount was found to be a 30-50 per cent excess. In another series of nitrations the amount of acetic acid used as solvent was varied from 3-7 times the weight of salicylaldehyde being nitrated. The optimum condition was found to be 4-5 times the weight of the aldehyde. Preparations using the best conditions of nitric acid concentration, excess of nitric acid and volume of acetic acid gave yields of 92 per cent of the combined 3- and 5-nitrosalicylaldehydes. Refinement of the method of separating the isomeric compounds gave consistent yields of the two isomers in the ratio of 3-nitro to 5-nitrosalicylaldehyde of 46 to 54. The details of this work will be found in Report XXIX. The recommended procedure for the nitration of salicylaldehyde, the separation of 3- and 5-nitro isomers and the preparation of di-(2-hydroxy-3-nitrobenzal) ethylenediimino cobalt follows.

Recommended Procedure for the Nitration of Salicylaldehyde and the Separation of the 3-Nitro and 5-Nitro Isomers. The Nitration. In a 5 liter, 3-neck flask, equipped with a motor driven stirrer, a dropping funnel, a thermometer, and a vacuum line to carry off the fumes, place 2000 g. of glacial acetic


Rate of Deterioration of
Di-(2-hydroxy-3-methoxybenzal)-ethylenediimine Cobalt
• Oxygen capacity of material in stationary bed machine.
• Oxygen capacity of material in rotating drum machine.
• Water content of material in rotating drum machine
6
5
4
3
2
1
0
1000
2000
3000
4000
5000
Number of Cycles

acid and 500 g. of salicylaldehyde (technical). Cool this solution in an ice bath to 25° and then start the slow addition of the nitric acid. During the next 2.5 hours add 400 g. of 98 per cent nitric acid, sp. gr. 1.50. This acid must be added slowly and after the first 100 g. has been added the temperature should be reduced to less than 15° and held below 15° until the addition is complete. After all of the acid has been added, remove the solution from the ice bath and allow it to warm to about 45°. This will take from 1-2 hours. When the temperature reaches 45°, immediately pour the material into 10 liters of water containing some cracked ice. Let the material stand at least 5 hours, then filter off and dry. The yield from this procedure is about 92 per cent, calculated on the basis of the technical grade salicylaldehyde as 85 per cent pure.

Separation of Isomers. On the basis of the work described in Report XV, the following procedure is recommended for the separation of 3-nitro salicylaldehyde from 5-nitro salicylaldehyde. Dissolve 4 parts of the mixture of isomers in 30 parts of water and 1 part of sodium hydroxide. Heat until all of the material is in solution, and allow it to cool slowly by standing overnight. Filter off the crystalline sodium salt of 5-nitro salicylaldehyde and treat the filtrate with 1:1 sulfuric acid until no more material is precipitated on further addition of acid. Filter off the pure 3-nitro salicylaldehyde.

In order to further purify the 5-nitro salicylaldehyde recrystallize the sodium 5-nitro salicylaldehyde twice from 6 times its weight of water. Dissolve the resulting pure sodium 5-nitro salicylaldehyde in 6 times its weight of water and acidify with 1 to 1 sulfuric acid until no more precipitate appears. Filter off and dry the pure 5-nitro salicylaldehyde.

In order to obtain the isomer of 3-nitro salicylaldehyde which will give an oxygen carrier dissolve the 3-nitro salicylaldehyde prepared above in twice its weight of hot alcohol and place the resulting solution in a well insulated container. Allow the solution to stand 2 or 3 days without disturbing and then filter off the large dark brown crystals of the high melting isomer. M.p. 108-110°.

(2) Recommended Procedure for the Preparation of Di-(2-hydroxy-3-nitrobenzal)ethylenediimine Cobalt. Dissolve 2 moles of 3-nitro salicylaldehyde (m.p. 108-110°) in 1500 ml. of hot 95 per cent alcohol. To this solution add 1 mole of ethylenediamine. Cool the solution and filter off the orange-yellow precipitate. Mix the Schiff's base without drying into 10 liters of hot water. Add 2 moles of sodium hydroxide and 2 moles of sodium acetate dissolved in 1 liter of water. To the resulting material add 2 moles of cobalt chloride dissolved in 1 liter of water. Digest

the mixture on a steam bath for 6 to 8 hours. Filter and dry the material at 100°. Activate the dried compound either in a vacuum oven at 120° or under infra-red lamps.

(3) The Activation of Di-(2-hydroxy-3-nitrobenzal)ethylenediimine Cobalt. Studies were made of the activation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt under various conditions. At a temperature of 125-130° in air the material was slowly activated, about 24 hours being required. There was no apparent decomposition at this temperature. Under a vacuum the compound was activated at a somewhat lower temperature. There did not seem to be a definite optimum temperature for the activation as experiments showed that the activation occurred very slowly at a temperature of 90° under a high vacuum. Only at a temperature of 120-125° was the rate of activation rapid.

The compound di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt was found to be partly activated at room temperature in a vacuum over phosphorus pentoxide. A sample activated in this manner for several days carried 2 per cent oxygen.

(4) Rate of Oxygenation of Di-(2-hydroxy-3-nitrobenzal)ethylenediimine Cobalt. A number of determinations of the rate of oxygenation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt were made by the gravimetric method described in detail in this report, Section X, Part C, subsection (1). This method was quite satisfactory although the compound exhibited a tendency to plug the glass wool filters and prevent the flow of gas through the U-tube.

It was found that di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt absorbed water as well as oxygen if the air or oxygen used was not throughly dried. Therefore a study was made to determine the correlation between the quantity of water present in the gas and the rate of oxygenation, the oxygen pressure and temperature being held constant. The humidity of the in-going gas was adjusted by passing the gas through sulfuric acid solutions of various concentrations or through suitable saturated salt solutions. The gain in weight of the U-tube was measured and the oxygen evolved and its volume determined. The weight of oxygen absorbed was then calculated and this weight of oxygen subtracted from the gain in weight of the U-tube. The difference in weight was then equal to the weight of water absorbed. The rate of absorption of water was assumed to be linear during the period of oxygenation, the rate of absorption of water per minute was calculated, and this value was applied as a correction to the weight of the U-tube at each interval during the oxygenation. There was thus obtained the rate of oxygenation plus hydration and the rate of oxygenation alone. Although this method may not be absolutely correct since the absorption of water may not have been linear, it is felt that any error involved could only be very small.

The data obtained for the rate of oxygenation plus hydration and the rate of oxygenation alone at atmospheric pressure and room temperature at relative humidites of 0, 5, 10 and 56 per cent are shown in the accompanying three graphs. A saturated zinc chloride solution was used to adjust the humidity of the air to 10 per cent; sulfuric acid of sp. gr. 1.67 was used to adjust the humidity to 5 per cent; the atmosphere as used directly had a humidity of 56 per cent.

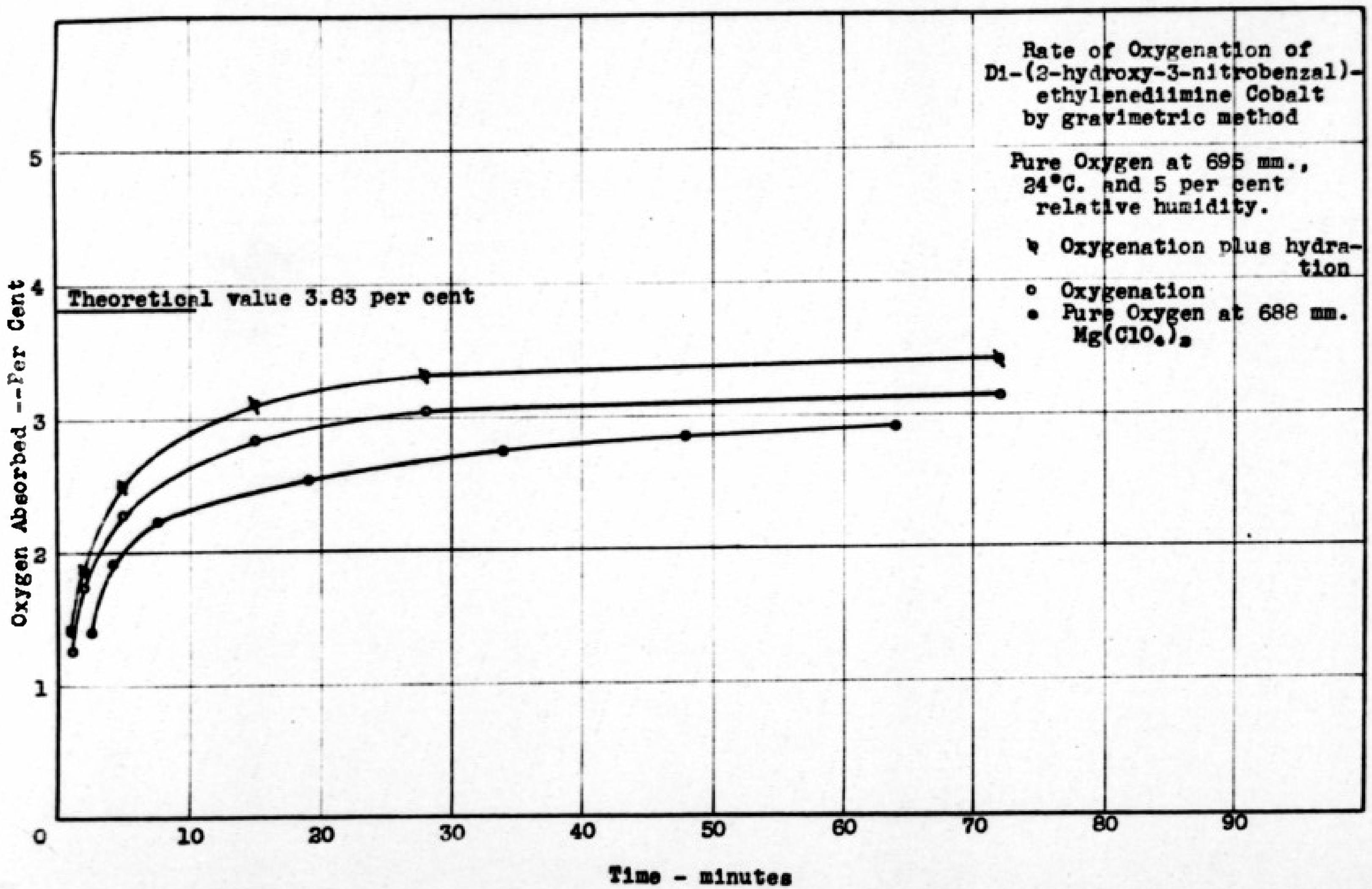
The rate of oxygenation of di-(2-hydroxy-3-nitrobenzal)-ethylenediimine cobalt in pure oxygen was also determined using the volumetric apparatus described in this report, Section X, Part C, subsection (3). The rates of oxygenation were determined at 24°, 55°, 70-72° and 87°. The results are shown graphically in the accompanying figure. The rate of oxygenation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt changed only slightly with temperature. This is particularly interesting since the rate of oxygenation of the parent, oxygen-carrying compound varies greatly with temperature.

The point at which the rate curve levels off depends markedly upon the oxygen pressure, that is, the higher the oxygen pressure the nearer to the theoretical, oxygen-carrying capacity the rate curve approaches before leveling off.

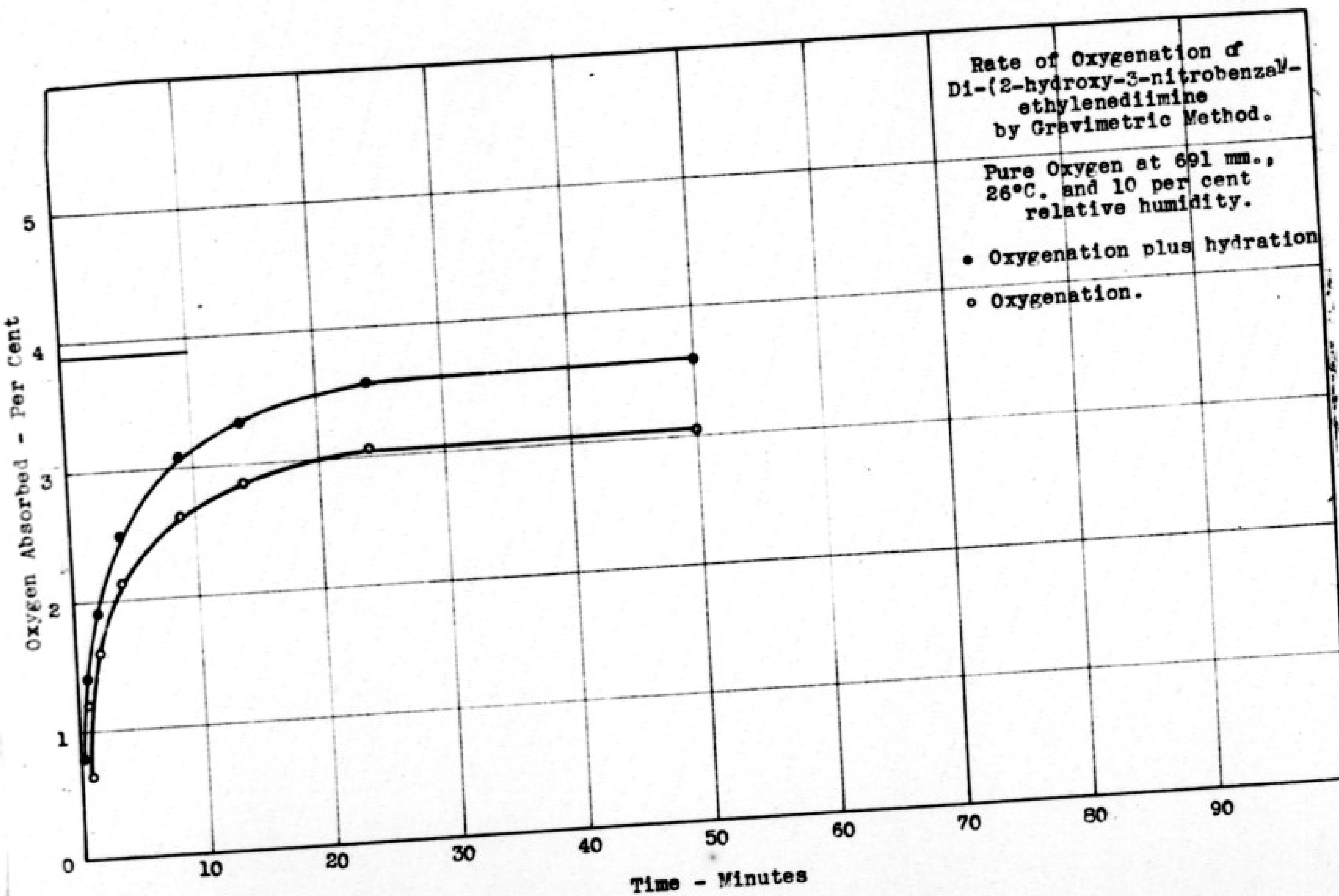
Even when deoxygenated di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt was placed in an atmosphere of oxygen at 200 psig., it did not quickly become entirely saturated with oxygen. In fact approximately 30 minutes was required for the last few tenths per cent of oxygen to be absorbed. However, when the compound was saturated with oxygen at 200 psig, it did not lose oxygen when the oxygen pressure was released.

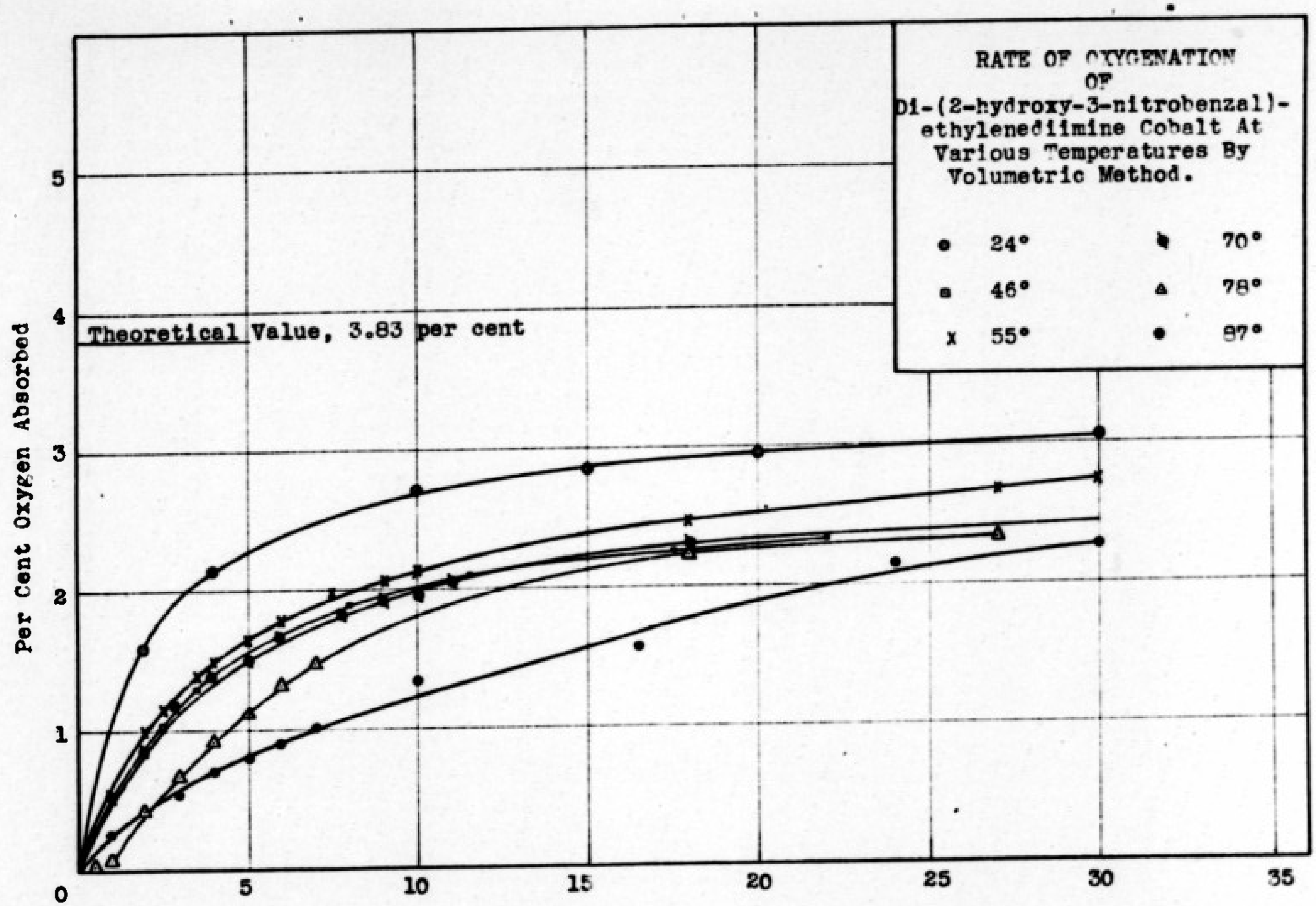
The role that water plays in the rate of oxygenation of di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt is not entirely clear. Apparently the rate of oxygenation is slightly faster in air or oxygen containing a small amount of water, that is, at relative humidities of 10 per cent or less. At the same time the compound is rendered inactive by the absorption of water. The deoxygenated compound upon absorption of water immediately turns yellow. It can be regenerated by heating in a vacuum at 120° as described in the following section.

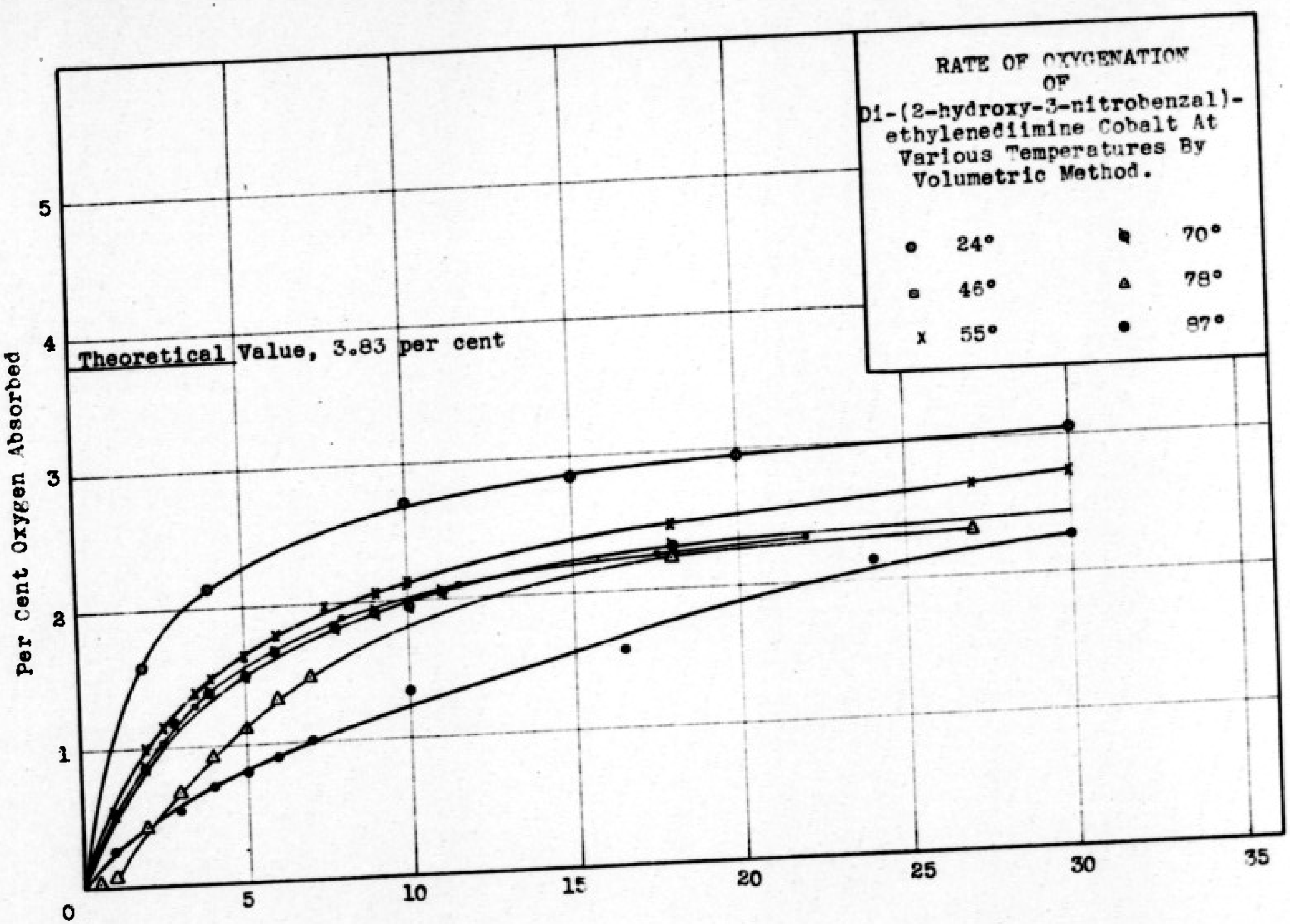
(5) <u>The Absorption of Moisture and of Oxygen by Di-(2-hydroxy-3-nitrobenzal)ethylenediimine Cobalt</u>. A series of weighed samples of the activated di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt were placed in air of various known humidities and allowed to come to equilibrium. The moisture content of the air ranged from 25 mg. to 0.2 mg. per liter of air; these humidities were obtained by placing in desiccators the proper concentration of sulfuric acid. At the end of 72 hours each sample was weighed, then deoxygenated and dehydrated by placing in an electrically heated tube at 150° and passing dry nitrogen over the sample.



Rate of Oxygenation of
Di-(2-hydroxy-3-nitrobenzal)-
ethylenediimine Cobalt
by gravimetric method
Pure Oxygen at 695 mm.,
24°C. and 5 per cent
relative humidity.
Oxygenation plus hydration
Oxygenation
Pure Oxygen at 688 mm.
$Mg(ClO_4)_2$
Theoretical value 3.83 per cent
Oxygen Absorbed --Per Cent
Time - minutes
0
1
2
3
4
5
10
20
30
40
50
60
70
80
90


Rate of Oxygenation of
Di-(2-hydroxy-3-nitrobenzal)-
ethylenediimine
by Gravimetric Method.
Pure Oxygen at 691 mm.,
26°C. and 10 per cent
relative humidity.
• Oxygenation plus hydration
∘ Oxygenation.
Oxygen Absorbed - Per Cent
Time - Minutes
0
1
2
3
4
5
10
20
30
40
50
60
70
80
90


RATE OF OXYGENATION
OF
Di-(2-hydroxy-3-nitrobenzal)-
ethylenediimine Cobalt At
Various Temperatures By
Volumetric Method.
24°
46°
55°
70°
78°
87°
Theoretical Value, 3.83 per cent
Per Cent Oxygen Absorbed
0
1
2
3
4
5
10
15
20
25
30
35



RATE OF OXYGENATION
OF
Di-(2-hydroxy-3-nitrobenzal)-
ethylenediimine Cobalt At
Various Temperatures By
Volumetric Method.
24°
46°
55°
70°
78°
87°
Theoretical Value, 3.83 per cent
Per Cent Oxygen Absorbed
0
1
2
3
4
5
10
15
20
25
30
35

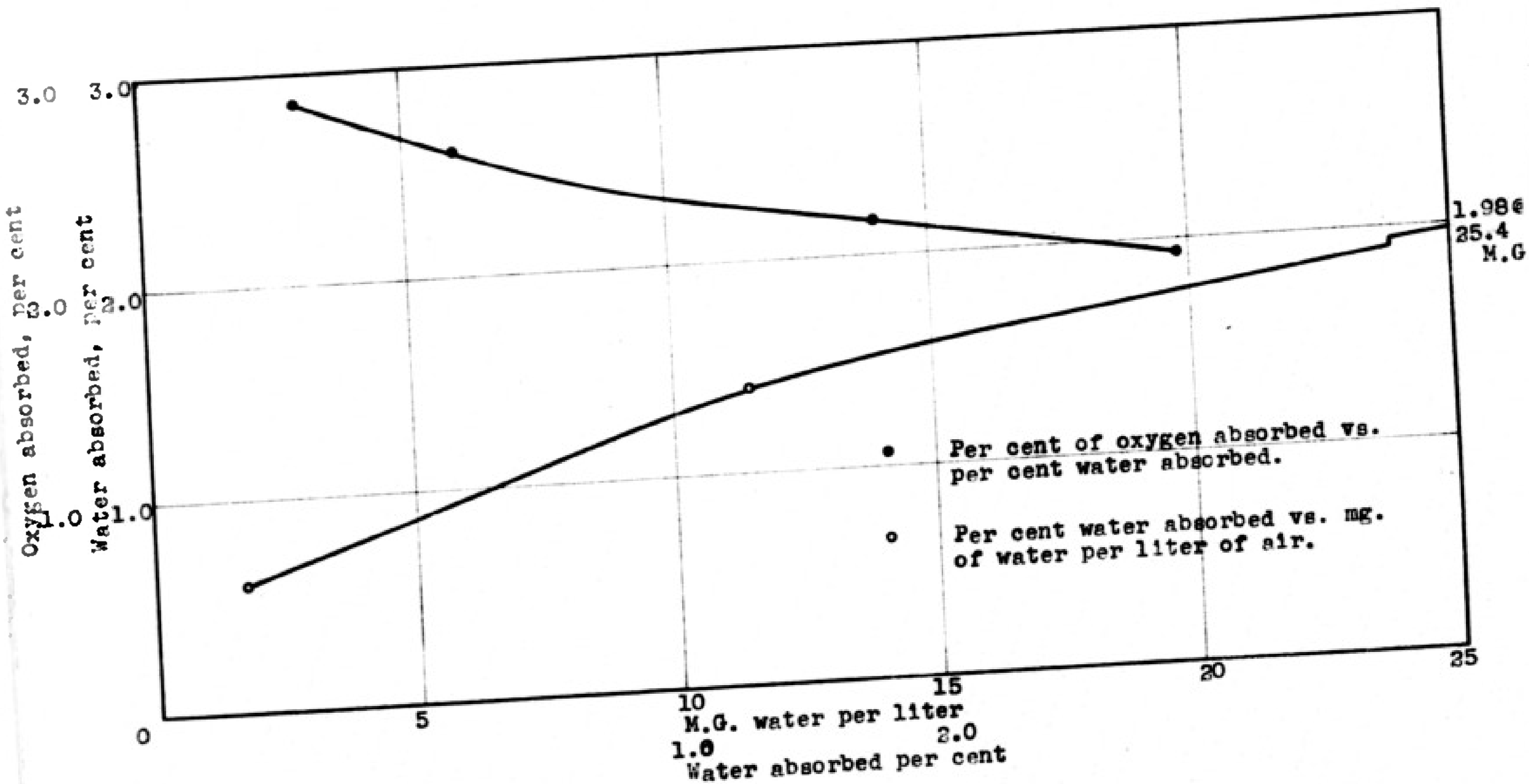
The moistura avolved was collected and weighed in a U-tube filled with magnesium perchlorate. The sample was then coolsd in a vacuum desiccator and reweighed. Tha loss in weight wes equivalent to both the oxygen and the moister absorbed. From the weight gained by the U-tube and the total loss in weight, the amount of moisture and the amount of oxygen absorbed at each humidity was calculated. The results obtained ere summarized in the following table and accompanying graph.

	Density H_2SO_4	Percent H_2SO_4	Mg. Water Per Liter Air	Par Cent Oxygen Absorbed	Per Cent Water Absorbed
I	1.299	39.6	25.4	1.93	1.98
II	1.450	55.5	11.4	2.16	1.40
III	1.521	62.1	6.4	---+	----+
IV	1.629	71.6	1.7	2.6	0.6
V	1.740	81.2	0.24	2.85	0.3

+ Sampla 3 was loat during the course of this run.

It is apparent that the absorption of oxygen decreased markedly with increasing water content in the eir. However, by comparison with similer data found for Co-Ox M, see thie raport, Section VI_2, Part B_2, eubsection (8) end accompanying graph, it is evident that the effect of moisturo on the 3-nitro compound is much less, than on the 3-methoxy compound.

In every caso upon deoxygenation and dehydration at 130° the samples returned to their original weight showing thet all of the moisture had been removed at thia temperature. The possibility of entirely removing absorbed moisture at a much lower temperature has not as yot been definitely ascertained.



Oxygen absorbed, per cent
Water absorbed, per cent
3.0
3.0
2.0
2.0
1.0
1.0
0
5
10
15
20
25
M.G. water per liter
1.0
2.0
Water absorbed per cent
1.986
25.4
M.G
Per cent of oxygen absorbed vs. per cent water absorbed.
Per cent water absorbed vs. mg. of water per liter of air.

I. 2-Hydroxy-3-nitro-5-methylbenzaldehyde.

The compound 2-hydroxy-3-nitro-5-methylbenzaldehyde wse obtained by the nitration of 2-hydroxy-5-methylbenzaldehyde in glacial acetic acid (Report XXXII, Section IV). Thia aldehyde was condenead with ethylenediamine and the yellow condensation product converted to a cobalt compound. This cobalt compound wae given the usual heat treatment and teete, and was found not to carry oxygen. This wae rather surprising inaemuch ae the 2-hydroxy-5-methylbenzaldehyde and 2-hydroxy-3-nitrobanzaldehyde compounds do carry oxygen.

J. 2-Hydroxy-3-phenylbenzaldehyde

Attempts were made to prepare the aldehyde 2-hydroxy-3-phenylbenzaldehyde by the Duff reaotion on o-hydroxybiphenyl. Tha dasired aldehyde was not obtained by steam dietillation of the acidified reaction mixture. Attempts to ieolata the aldehyde by extraction methods were not made and other methode of synthesis have not as yet been employed.

K. 2-Hydroxy-5-phenylbenzaldehyde

The compound 2-hydroxy-5-phenylbenzaldehyde was eynthesized from p-hydroxybiphenyl by the Duff reaction. Thie aldehyde was condensed with ethylenediamine and the bright yellow Sohiff's base obtained converted to a cobalt derivative. Attempts to activate this material by heating in a vacuum at various temperatures proved unsuccessful and the material did not carry oxygen. For details of the preparation of the aldehyde see Report XXXII, Section V.

L. 2-Hydroxy-4, 6-dimethylbenzaldehyde

The above aldehyde was prepared by the Duff reaction on 3,5-xylenol. Upon steam distillation of the acidified reaotion mixture the desired aldehyde was obtained as a white solid, m.p.: 43-45°. Yield: 11 per cent. The Schiff's baac of the above aldehyde with ethylenediamine was prepared by the usual method. The cobalt derivative was prepared by the alcohol method and yielded a brilliant orange-red compound. Upon heating in a vacuum at temperaturea varying from 100-170° there was no appreciable decrease in weight or change in color, and the samplo showed no oxygen activity.

M. 2,3-Dihydroxybenzaldehyde.

A great deal of work was devoted to the preparation of this material by the demethylation of 2-hydroxy-3-methoxybenzaldehyde.

(1) Synthesis from 2-Hydroxy-3-methoxybenzaldehyde by Demethylation. The demethylation of 2-hydroxy-3-methoxybenzaldehyde would appear to be a relatively simple matter particularly in view of the ease with which demethylations are ordinarily carried out and in view of the work by Pauly (Ann., 383, 312, 1911) who reported obtaining a 50 per cent yield of 2,3-dihydroxybenzaldehyde by demethylating 2-hydroxy-3-methoxybenzaldehyde with 48 per cent hydrobromic acid in an acetic acid solution. This reaction was also carried out by Gates at Stanford University, (Master's Thesis). Some 15 different attempts were made to carry out this reaction using hydrobromic acid and the procedures of Pauly and of Gates, but the results were far from satisfactory. The yields never exceeded 15 per cent cent and the amount of labor involved in working up the product and separating it from the unreacted 2-hydroxy-3-methoxybenzaldehyde and from the tar which accompanies the reaction discouraged any hope of making this process a practical one.

The Monsanto Chemical Company has prepared 2,3-dihydroxybenzaldehyde. They stated, however, without telling the method used, that the material was extremely difficult to obtain..

(2) Condensation with Ethylenediamine and Cobalt. Several preparations of di-(2,3-dihydroxybenzal)ethylenediimine were made by the usual procedure of preparing a Schiff's base. This work was done with a sample of 2,3-dihydroxybenzaldehyde obtained from the Monsanto Chemical Company. 2,3-Dihydroxybenzaldehyde was dissolved in hot alcohol and to this solution one-half equivalent of ethylenediamine was added. With the proper concentration a red solution was formed which on cooling formed a yellow-orange precipitate consisting of flat plate like crystals. This material had a sharp decomposition temperature at 220°. When prepared by this method recrystallization did not appear to improve the product.

The reaction of di-(2,3-dihydroxybenzal)ethylenediimine and cobalt salts was carried out a number of times. This compound was prepared by first forming a solution of the sodium salt of the condensation product, then adding cobalt chloride. Various modifications of this method in which alcohol was used were also tried. The pyridine method of Calvin and the direct mixing method were also employed. In all these preparations the product was red-brown in color after having been dried at 100°. The material did not carry oxygen. On heating to temperatures as high as 200° in a high vacuum the material did not lose appreciably in weight and did not exhibit oxygen-carrying properties.

When prepared in high concentrations of alcohol an orchid material was obtained which appeared to be a comoound corresponding to the orange compound formed by the reaction of disalicylalethylenediimine, sodium hydroxide, and cobalt chloride in absolute alcohol. This material did not react with water, however.

It was believed that di-(2,3-dihydroxybenzal)ethylenediimine cobalt, which has two acidic hydroxy groups, could form a soluble salt with a base and produce an oxygen carrier which might work in water solution. A number of attempts were made to isolate the sodium salt without success. The di-(2,3-dihydroxybenzal)ethylenediimine cobalt was found to be soluble to the extent of 3 per cent in water containing 2 equivalents of sodium hydroxide. This water solution was found not to carry oxygen. When oxygen was bubbled through this solution it turned black, showing possible oxidation. The materials recovered from the solution, etiher before or after treatment, were found not to carry oxygen.

N. 2-Hydroxy-3-ethoxybenzaldehyde

The work on di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt described in Section VI, part B_2 of this report has shown that this compound oxygenates extremely rapidly in air at atmospheric pressure and at temperatures between 0° and 15°. Naturally the character of the homologous 3-alkoxy compounds became of interest. An increase in molecular weight was predicted by Latimer to increase the general reactivity of the parent oxygen-carrying compound and in turn to increase the rate of oxygenation. The methoxy compound is fast, but a faster compound would be still better. In addition the methoxy compound has certain undesirable characteristics. It is first obtained with water of crystallization which can only be eliminated by heating the material to 170° in a vacuum, thus complicating its manufacture. The activated material is extremely hygroscopic in nature so that the air used to oxygenate the comoound must be extremely dry. The absorption of water decreases the oxygen carrying capacity of the compound since the hydrated material does not carry oxygen. A more desirable compound would give up its water at a temperature below 100° and thus render the activation step at a higher temperature unnecessary and in addition allow the use of air not so thoroughly dried.

The cobalt drivative of 2-hydroxy-3-ethoxybenzaldehyde and ethylenediamine was therefore prepared and since it appeared not to have some of the undesirable characteristics of the methoxy compound it was subjected to detailed studies which are continuing as this report is written.

Synthetic 2-hydroxy-3-methoxybenzaldehyde was available in fairly large quantities for the preparation of Co-Ox M; unfortunately, sufficient quantities of 2-hydroxy-3-ethoxybenzaldehyde were not available for preliminary work on its cobalt compound. The early work was carried out with 2-hydroxy-3-ethoxybenzaldehyde prepared from catechol by conversion to o-ethoxyphenol and the application of the Duff reaction on the latter. Later, attempts were made to synthesize 2-hydroxy-3-ethoxybenzaldehyde by demethyleting 2-hydroxy-3-methoxybenzaldehyde and ethylating the 2,3-dihydroxybenzaldehyde so produced. Difficulties were experienced with both steps of this method and it does not appear to be a feasible method for obtaining 2-hydroxy-3-ethoxybenzaldehyde. It was known that the Monsanto Chemical Company of St. Louis, Missouri manufactured ethylvanillin and it was therefore suspected that they might have available, as a by-product, 2-hydroxy-3-ethoxybenzaldehyde. Although at first reluctant to discuss 2-hydroxy-3-ethoxybenzaldehyde because they had not devoted attention to working up the crude material they had available, later they furnished samples of crude 2-hydroxy-3-ethoxybenzaldehyde for experimental work. Monsanto stated further that the production of 2-hydroxy-3-ethoxybenzaldehyde was limited to about 200 pounds per month and that there was no known method of preparing the material. It would appear, however, that a method of producing this material could be devised if the effort required were justified. The following subsections describe in detail the work which was done on the synthesis of 2-hydroxy-3-ethoxybenzaldehyde.

(1) Synthesis from Catechol.

(a) Synthesis of o-Ethoxyphenol. Although o-ethoxyphenol is mentioned in the literature a great many times, clear cut directions for its synthesis are lacking. The di-ethyl ether has been made and then converted to the mono-ethyl ether by treatment with alkali. Very early work is mentioned in which the ethylation is carried out using ethyl iodide but no details are given. Another method is described in which o-ethoxyphenol is obtained from o-phenetidin by diazotization. Still another method describes a preparation from the di-ether by means of a Grignard reaction. A review of this literature will be found in Report XXXVII, Section III.

A great number of preparations of this material were carried out during the course of the work and the variables which were considered important in the preparation, were varied systematically. The temperature during the addition of the sodium hydroxide to the pyrocatechol was varied from 5°C to 40°C and the length of time taken to add the sodium hydroxide was varied from 20 to 60 minutes. The temperature of the solution during the addition of ethyl sulfate was varied from 50° to 85° and the time of addition from 35 to 60 minutes. The final solution was refluxed for periods varying from 15 minutes to 120 minutes.

Recommended Procedure for the Preparation of o-Ethoxyphenol.

In a liter, 3-necked, round-bottom flask provided with a reflux condenser, a stirrer, and a dropping funnel, mix 1 mole (110 g.) of pyrocatechol with 200 ml. of water. In a beaker dissolve 1 mole (40 g.) of sodium hydroxide in 100 ml. of water. Heat the pyrocatechol solution to boiling with constant stirring. When it is refluxing evenly and all of the air has been displaced from the flask, add the sodium hydroxide solution through the dropping funnel. Rinse the funnel with a little distilled water and then pour 158 g. (4 g. excess) of diethylsulfate into it. Add this diethylsulfate slowly to the refluxing solution over a period of 45 minutes. Reflux the final mixture for one hour, cool, acidify, and separate the top (oily) layer. Steam distill this oil with a small flame under the flask. Then separate the oil from the distillate, dry for a few hours over anhydrous calcium sulfate and vacuum distill. Collect a 5 degree fraction at about 100° under 10 mm. pressure.

The unreacted pyrocatechol can be recovered from the water layer of the original reaction mixture by extraction with ether. Evaporate the ether and vacuum distill the residue, collecting the pyrocatechol above 110° under 10 mm. pressure.

(b) Application of the Duff Reaction to o-Ethoxyphenol.

Of the various methods available for the preparation of o-hydroxy aldehydes, the method of Duff (J. Chem. Soc., 1941, 547) is particularly interesting in being rapid and easy to carry out. Although previous experience with the method had not been too favorable, see Report XXXII, it was decided to study the reaction somewhat further. For this reason studies were made on o-phenylphenol, 3,5-dimethylphenol, and p-cresol. The effect of drying the reagents was studied. The important point, however, was found to be the temperature at the time of adding the hexamethylenetetramine, and it was found best to add the hexamethylenetetramine and phenol simultaneously. This reaction was run a number of times in the preparation of 2-hydroxy-3-ethoxybenzaldehyde with various modifications in the procedure but the maximum yield obtained was only 11 per cent. (See Report XXVII, Section V for details of this work.)

2-Hydroxy-3-ethoxybenzaldehyde is a white crystalline solid (m.p.: 64-65°, b.p. 263-264°/740 mm. with slight decomposition.)

(2) Synthesis by Ethylation of 2,3-Dihydroxybenzaldehyde. It was thought that on ethylation the 3- position of 2,3-dihydroxybenzaldehyde would be relatively easy to ethylate without the simultaneous ethylation of the 2- position and that in this manner 2-hydroxy-3-ethoxybenzaldehyde could be prepared. A number of unsuccessful attempts were made to ethylate 2,3-dihydroxybenzaldehyde using both diethyl sulfate and ethyl

iodide and carry the reaction out with aqueous sodium hydroxide solution, alcoholic sodium hydroxide solution and with metallic sodium in toluene. From all of these variations, only the original 2,3-dihydroxybenzeldehyde was obtained with sometimes a small amount of tar. These negative results were rather disconcerting and are rather difficult to explain. They are possibly due to a double chelate structure of 2,3-dihydroxybenzaldehyde.

(3) Isolation from Monsanto Crude. A ten pound sample of crude 2-hydroxy-3-ethoxybenzaldehyde was obtained from the Monsanto Chemical Company with the warning that it would be very poor material containing only about 60 per cent of 2-hydroxy-3-ethoxybenzaldehyde. The material obtained was subjected to a vacuum distillation. The 2-hydroxy-3-ethoxybenzaldehyde distilled at 156-158°/30 mm., yielding about 80 per cent of material melting at 64°. The fraction distilling at 158-185° was further fractionated yielding a further 10 per cent of 2-hydroxy-3-ethoxybenzaldehyde. A small amount of higher boiling material was obtained.

Additional studies on the crude material have indicated that the Schiff's base with ethylenediamine prepared directly from the crude material has the same melting point as a sample of recrystallized Schiff's base prepared from carefully purified aldehyde and ethylenediamine. This would indicate that there is no necessity for further purifying the material if the Schiff's base is isolated as a step in the manufacture of the cobalt compound.

(4) Di-(2-hydroxy-3-ethoxybenzal)ethylenediimine. 2-Hydroxy-3-ethoxybenzaldehyde was condensed with ethylenediamine in an absolute alcohol medium. The bright yellow condensation was recrystallized once from alcohol m.p. 138-140°. The Schiff's base was soluble in dilute alkali.

(5) Di-(2-hydroxy-3-ethoxybenzal)ethylenediimine Cobalt (Co-Ox ET). The first preparation of di-(2-hydroxy-3-ethoxybenzal)ethylenediimine cobalt was made in dilute alcohol. The Schiff's base was dissolved in hot alcohol and treated with a hot, aqueous solution of the calculated amount of cobalt acetate. A golden precipitate was obtained. This material turned brownish-red when dried under vacuum at 100°. When the dried material was exposed to air, it quickly turned black. The compound carried the theoretical amount of oxygen, 3.80 per cent.

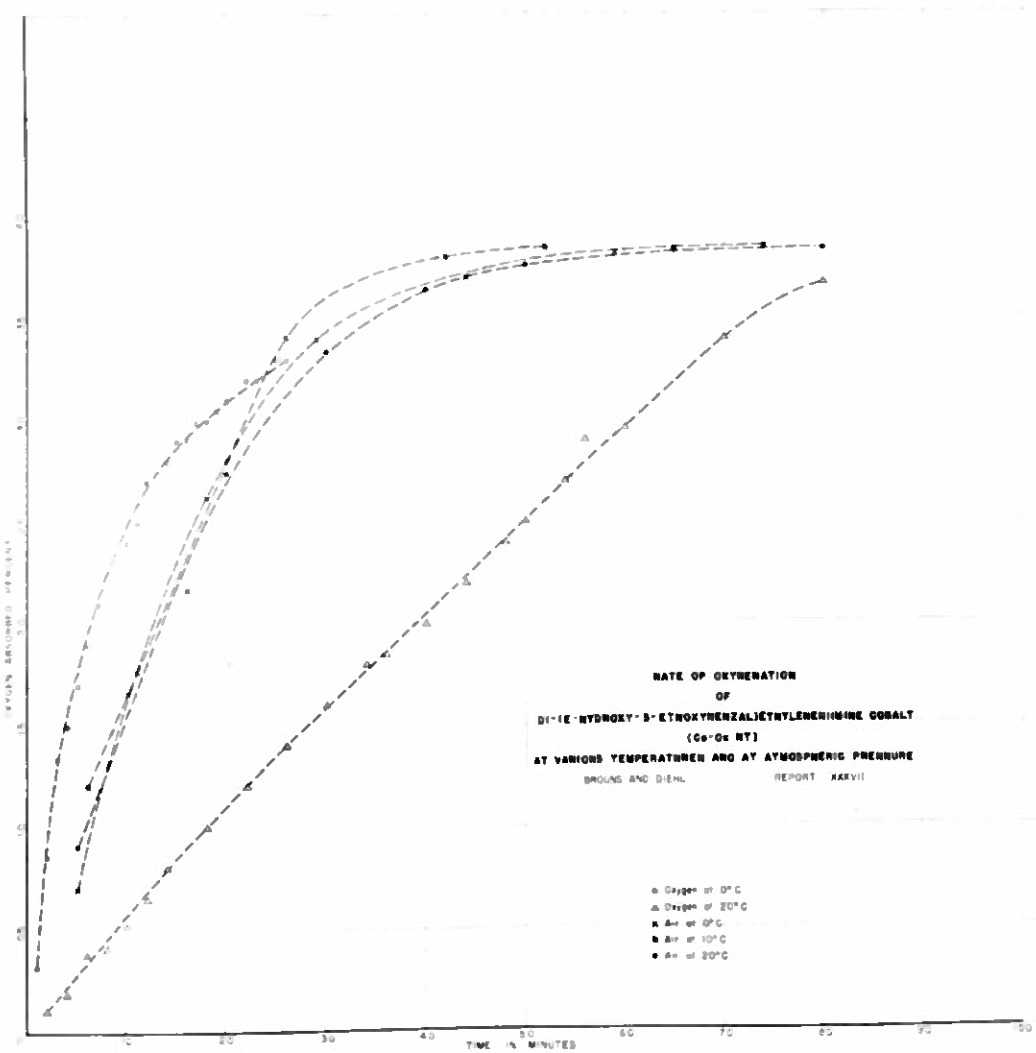
The second batch of di-(2-hydroxy-3-ethoxybenzal)ethylenediimine cobalt was also prepared in dilute alcohol but using the sodium salt of the Schiff's base. The Schiff's base prepared from 2-hydroxy-3-ethoxybenzaldehyde was dissolved in the dilute alkali and then treated with cobalt acetate to form di-(2-hydroxy-3-ethoxybenzal)ethylenediimine cobalt. This was carried out in a 30 per cent alcohol solution buffered with enough acetic acid and sodium acetate to make the final mixture slightly acid. The compound was maroon-red but drying at 100° changed this color to a light reddish-brown. However, as soon as the compound was cooled and exposed to air it turned black very rapidly. This color change was checked on the m.p. apparatus and was found to occur at 87-90°. The oxygen absorbing capacity of this material corresponded to its theoretical value of 3.80 per cent.

(6) Rate of Oxygenation of (Di-(2-hydroxy-3-ethoxybenzal)-ethylenediimine Cobalt. The rate of oxygenation of di-(2-hydroxy-3-ethoxybenzal)ethylenediimine cobalt was determined at three temperatures, 0°, 10°, and 20°, using the gravimetric method described in Section X, Part C, Subsection (1) of this report. The rate of oxygenation was essentially the same at each of these temperatures and the rate of oxygenation is somewhat slower than that of the methoxy compound, reaching 80 per cent of saturation in 21 minutes, whereas the methoxy compound reaches 80 per cent of saturation in less than 10 minutes. The results of these studies are presented in the accompanying graph. The rate of oxygenation was also determined in pure oxygen at 26° at a pressure of 8 psig using the differential manometric apparatus described in Section X, Part A of this report; the oxygenation was 80 per cent complete in 1 minute and completely saturated in 5 minutes. It thus appears that the rate of oxygenation of the ethoxy compound is rather independent of the temperature but greatly affected by changes in oxygen pressure at pressures about atmospheric. The rate of oxygenation in air at 5°, 14°, 30°, and 35° at atmospheric pressure was also determined using the manometric rate apparatus (this report, Section X, Part C, Subsection (2)) and practically the same results obtained as given in the accompanying graph.

See Section X, Part C for a comparison of the rates of oxygenation of the ethoxy and other compounds.

(7) Hygroscopisity and Dehydration of Di-(2-hydroxy-3-ethoxybenzal)ethylenediimine Cobalt. When Co-Ox BT was allowed to absorb oxygen freely from air it was found to gain more than theoretical weight. A check on the moisture content of such sample which had been standing in air having a humidity of 80-90 per cent proved that the compound had absorbed 3.4 per cent water and 1.8 per cent oxygen. On exposure for 40 hours to air having a humidity of 27 per cent it absorbed 2.6 per cent water and 1.6 per cent oxygen.

A sample of the compound that had been allowed to absorb water and oxygen freely from air was heated in air at 115°. Analysis showed that after this treatment for several hours the compound still contained almost 1 per cent water but no oxygen.


RATE OF OXYGENATION
OF
DI-(2-HYDROXY-3-ETHOXYBENZAL)ETHYLENEDIIMINE COBALT
(Co-Ox ET)
AT VARIOUS TEMPERATURES AND AT ATMOSPHERIC PRESSURE
BROUNS AND DIEHL
REPORT XXXVII
Oxygen at 0°C
Oxygen at 20°C
Air at 0°C
Air at 10°C
Air at 20°C
OXYGEN ABSORBED PERCENT
TIME IN MINUTES
0
10
20
30
40
50
60
70
80
90
100

However, all of the water was easily removed at 110° under a vacuum or in a stream of dry nitrogen gas.

The compound which still contained 1 per cent moisture continued to absorb the theoretical amount of oxygen when placed under pressure in the oxygen bomb. Studies on the effect of moisture content on the rate of oxygenation are still in progrsss.

O. 2-Hydroxy-3-n-propoxybenzaldehyde.

The compound 2-hydroxy-3-n-propoxybenzaldehyde is not described in the literature but previous work with the monoethyl ether of pyrocatechol and the Duff reaction indicated that this general method could be used to prepare the homologs of 2-hydroxy-3-ethoxybenzaldehyde.

(1) Synthesis from Catechol. o-n-Propoxyphenol was prepared from pyrocatechol in the same way that o-ethoxyphenol was prepared, but with slightly smaller yields. (See Section VI., Part N, subsection (1), article (a)).

The o-n-propoxy phenol was converted to 2-hydroxy-3-n-propoxybenzaldehyde by the Duff reaction. In this processs the steam distillation was found to be impractical so the final reaction mixture was diluted with water and extracted well with ether. The compound was obtained by distillation from this ether extract in 15 per cent yields.

2-Hydroxy-3-n-propoxybenzaldehyde was found to be a liquid at room temperatures and to have a boiling point of 135°/12 mm. The density was found to be 1.116 at 25°. The refractive indsx was found to be 1.546 at 25°. The phenylhydrazone was yellow, and melted at 109-110°.

(2) Condensation with Ethylenediamine. 2-Hydroxy-3-n-propoxybenzaldehyde was condensed with ethylenediamine in an alcohol medium by ths usual procedure. A bright yellow, crystalline material was obtained, which was recrystallized from alcohol. M.p.: 93-94°; yield: quantitative.

(3) Di-(2-hydroxy-3-n-propoxybenzal)ethylenediimine Cobalt. Di-(2-hydroxy-3-n-propoxybenzal)ethylenediimine cobalt was prepared from the Schiff's base by the usual alkali method using about 30 per cent alcohol. The precipitate was brown and upon drying under a vacuum at 110° it carried 3.5 per cent, corresponding to the theoretical amount of oxygen. The deoxygenation temperature was found to be about 95°.

The compound was found to be very hygroscopic. It became sticky on exposure to air. This unfortunate characteristic interfered greatly in the studies made on the material.

(4) Rate of Oxygenation of Di-(2-hydroxy-3-n-propoxybenzal)-ethylenediimine Cobalt. An attempt was made to determine the rate of oxygenation of di-(2-hydroxy-3-*n*-propoxybenzal)ethylenediimine cobalt in air at atmospheric pressure by the gravimetric method (Section X, Part C, subsection (1)). The compound packed in the tube and air could not be drawn through it rapidly enough. The compound was then pelleted, but several trials at 20° failed to give consistent results.

The rate of oxygenation was also determined in pure oxygen using the differential manometric apparatus, and found to be the greatest of any compound hitherto studied. It reached 90 per cent saturation in two minutes in pure oxygen. See Section X, Part C for these results.

P,Q,R,S,T,U,V,W. Various 2-Hydroxy-3-alkoxybenzaldehydes.

The following 2-hydroxy-3-alkoxybenzaldehydes are in various stages of preparation: 2-hydroxy-3-*iso*-propoxybenzaldehyde, 2-hydroxy-*3*-*n*-butoxybenzaldehyde, 2-hydroxy-3-*sec*-butoxybenzaldehyde, 2-hydroxy-3-*tert*-butoxybenzaldehyde, 2-hydroxy-3-*iso*-butoxybenzaldehyde, 2-hydroxy-3-*n*-amyloxybenzaldehyde, 2-hydroxy-3-allyloxybenzaldehyde, and 2-hydroxy-3-B-ethoxyethoxybenzaldehyde. The work on these compounds has not progressed far enough to warrant detailed consideration at this time.

X. 2,4-Dihydroxybenzaldehyde

Y. 2-Hydroxy-4-methoxybenzaldehyde

Z. 2,5-Dihydroxybenzaldehyde

The above aldehydes are in various stages of preparation. The work on these compounds has not progressed far enough at this time to warrant a more detailed discussion of the work.

AA. 2-Hydroxy-5-methoxybenzaldehyde

2-Hydroxy-5-methoxybenzaldehyde was prepared by the Duff reaction on p-methoxyphenol. This phenol was synthesized by two methods, one involving the action of methyl iodide and the other dimethyl sulfate on hydroquinone in an alkaline solution. The yields by both methods were 40 per cent.

The Duff reaction on the p-methoxyphenol was carried out in several small batches. The aldehyde steam distilled as a yellow oil: m.p.: 4°. Yield: 16-18 per cent. The phenylhydrazone of this aldehyde was prepared and recrystallized from alcohol and from ligroin: m.p.& 139.5°. The Schiff's base of this aldehyde and ethylenediamine was prepared by condensation in absolute alcohol and was obtained as a crystalline, yellow material, m.p.: 163°. These two derivatives of this aldehyde have not been reported in the literature.

The cobalt derivative of the Schiff's base was prepared by three different methods. In each case a red-brown compound was obtained. This material was heated in a vacuum at various temperatures and then tested for oxygen absorption by exposure to oxygen at 175 psig. None of the preparations carried oxygen. Details of this work may be found in Report XLVII.

AB. 2-Hydroxy-5-ethoxybenzaldehyde

2-Hydroxy-5-ethoxybenzaldehyde was prepared from p-ethoxyphenol by the Duff reaction. The p-ethoxyphenol used was prepared by the action of ethyl iodide on hydroquinone in alkaline solution and also by the action of diethyl sulfate on hydroquinone in alkaline solution. Yields of about 35 per cent were obtained in these ethylations.

The Duff reaction proceeded in the normal manner and yields of 16-18 per cent were obtained. 2-Hydroxy-5-ethoxybenzaldehyde was obtained as a light yellow crystalline material; m.p.: 48-49°, reported by Hantzsch (J. prakt. Chem., (2), 22, 464): 51.5°.

The aldehyde was condensed with ethylenediamine in absolute alcohol, yielding a bright yellow compound; m.p.: 150-152°. The cobalt derivative of this condensation product was prepared by three methods. A red-brown product was obtained in each case; the preparations did not carry oxygen either after having been dried at 100° or heated at higher temperatures. This work is described in detail in Report XLVIII.

AC. 2-Hydroxy-3-aminobenzaldehyde

Several preparations of 2-hydroxy-3-aminobenzaldehyde were made by the reduction of 2-hydroxy-3-nitrobenzaldehyde (3-nitrosalicylaldehyde) with stannous chloride in concentrated hydrochloric acid solution. The 2-hydroxy-3-aminobenzaldehyde was first isolated as the hydrochloride of its tin salt and was then converted to the amine hydrochloride by hydrolysis. All attempts to condense this material with ethylenediamine failed. 2-Hydroxy-3-aminobenzaldehyde apparently reacted with itself as rapidly as with ethylenediamine when the hydrochloride was neutralized. Some evidence of the formation of the Schiff's base with ethylenediamine was obtained but none of the material could be isolated. This work is described in detail in Report XLI.

AD. 2-Hydroxy-3-bromobenzaldehyde

A small amount of 2-hydroxy-3-bromobenzaldehyde was obtained by the Gattermann decomposition of the diazonium salt resulting from the treatment of 2-hydroxy-3-aminobenzaldehyde hydrochloride with sodium nitrite in cold, acid solution. The aldehyde was recrystallized from water; m.p.:49.5-50°, reported by Muller (Ber., 42, 3700): 49°. The Schiff's base of the aldehyde and ethylenediamine was prepared in the usual manner and converted to the cobalt salt by three methods. The products ranged in color from dark yellow to deep red-brown. On high temperature drying they did not change color. They did not carry oxygen. Details of this work are given in Report XLI.

AE. Acetylacetone

AF. Benzoylacetone

Quantities of acetylacetone and benzoylacetone have been made and condensed with ethylenediamine by methods previously described in the literature. Preliminary investigations of the properties of the cobalt compounds of these two Schiff's bases are being carried out. The work has not progressed far enough as yet to warrant a detailed discussion.

AG. Dibenzoylmethane

Dibenzoylmethane was prepared from benzalacetophenone dibromide and sodium methylate according to the directions given in Organic Syntheses, Collective Volume I, 2nd Ed., p. 205. The benzalacetophenone dibromide was prepared by brominating benzalacetophenone. The benzalacetophenone was prepared from acetophenone and benzaldehyde by the method described in Organic Syntheses, Collective Volume I, 2nd Ed., p. 48.

An unsuccessful attempt was made to condense dibenzoylmethane with ethylenediamine in hot absolute alcohol. In other attempts to effect the condensation, alcohol solutions of the two reagents were refluxed for varying periods of time; no condensation was effected. Even refluxing in 96 per cent ethylenediamine followed by neutralization was of no avail.

In other attempts, barium oxide and anhydrous calcium sulfate were added to an alcohol solution of the reactants and the mixture refluxed; even these dehydrating agents failed to effect the condensation. A small yield of yellow needles was obtained which failed to dissolve in sodium hydroxide, and analysis showed no nitrogen to be present; therefore, the desired condensation product was not obtained.

AH. Formylcamphor.

The compound formylcamphor contains a keto group adjacent to an aldehyde group, and has been shown to enolize yielding an acid hydroxyl group which will form metal salts. In the enol form this structure is similar to that found in the aromatic o-hydroxyaldehydes. This compound was synthesized and the cobalt derivative of its Schiff's base with ethylenediamine was prepared. The first step in the synthesis involved the preparation of iso-amylformate by the esterification of iso-amyl alcohol and formic acid using dry hydrogen chloride as a catalyst. In the second step, formylcamphor was obtained by the reaction of iso-amylformate and camphor in the presence of metallic sodium using dry ether as a solvent. The details of the work with formylcamphor will be found in Report XLV, Section V.

(1) Condensation with Ethylenediamine and the Cobalt Derivative. The Schiff's base of formylcamphor with ethylenediamine was prepared using a hot methyl alcohol solution of the two compounds. This condensation product was a light yellow crystalline material, m.p.: 215°. The cobalt derivative was prepared by the usual alcohol method and an orchid colored, crystalline material was obtained, which melted with decomposition at 190-200°. This compound showed no oxygen activity when activated by the usual methods.

(2) Condensation with o-phenylenediamine and the Cobalt Derivative. The formylcamphor was condensed with o-phenylenediamine by adding a hot alcohol solution of the diamine to a hot alcohol solution of the formylcamphor. A yellow Schiff's base was obtained which was recrystallized from 50 per cent alcohol, m.p.: 125°. The cobalt compound was prepared using the alcohol method and was obtained as a dark brown compound. This material did not absorb oxygen following activation by heating in a vacuum at several temperatures up to 170°.

AI. o-Aminobenzaldehyde

It was decided that a possible substitute for salicylaldehyde in the preparation of oxygen carriers might be o-aminobenzaldehyde. Pfeiffer (J.prakt. Chem. (2) 149, 217, (1937)) reported that o-aminobenzaldehyde yielded a Schiff's base with ethylenediamine and that the latter gave copper and nickel derivatives similar to the corresponding compounds from salicylaldehyde. o-Aminobenzaldehyde is not on the market and a search of the literature revealed that the only practical laboratory method of preparation is that of Thiele and Winter (Ann., 311, 356 (1900)), involving the oxidation of o-nitrotoluene to o-nitrobenzaldehyde and the reduction of the latter to o-aminobenzaldehyde by ferrous sulfate in a sodium carbonate solution.

Considerable difficulty was encountered in carrying out the oxidation of o-nitrotoluene, a reaction carried out in acetic acid with chromic oxide. The o-nitrobenzaldehydediacetate was apparently hydrolyzed and further oxidized. It was found that by using redistilled acetic anhydride and no acetic acid in the preparation the oxidation could be carried out quite satisfactorily. Only about 0.5 g. of the diacetate has been prepared and as yet no attempt has been made to hydrolyze and reduce this material. This work is being continued.

VII. Compounds of Structure Different From the Parent Compound.

D. Hexa-allylamine peroxodihydroxodicobalt Trichloride

The field of the polynuclear cobalt compounds, extensively worked by Werner early in the present century, offers an intriguing region for study in the effort to discover oxygen carrying chemicals and to explain the mechanism of the oxygen-carrying process of the carriers now known. Unfortunately the literature of this field is badly clouded with incorrect and uncorrelated work and a great effort will be required to straighten and organize the jumbled mass of material. Preliminary skirmishes into the field, both at California and at Iowa State College, notably in the preparation and testing of Vortmann's sulfate, did not immediately yield results of promise.

About the only work during the last twenty five years on the polynuclear compounds is that of Bucknall and Wardlaw (J. Chem. Soc., 1928, 2648) and of Percival and Wardlaw (J. Chem. Soc., 1929, 1317) who prepared compounds containing allylamine, propylamine and benzylamine. These compounds contained peroxo bridges and although no suggestion was made that the oxygen in the compounds might be carried reversibly they appeared worth investigating. The allylamine compound,

$$\left[3C_3H_5NH_2\ Co \begin{matrix} O - O \\ - OH - \\ OH \end{matrix} Co\ 3C_3H_5NH_2 \right] Cl_3$$

Hexa-allylamineperoxodihydroxodicobalt trichloride appeared to be the best characterized of the compounds described and was accordingly prepared and investigated.

The synthesis was carried out without difficulty following the directions of Bucknall and Wardlaw. Repeated attempts were made to deoxygenate the material at various temperatures and in a vacuum, but the peroxo group could not be expelled. Heating at higher temperatures caused slow decomposition of the material with the evolution of allylamine. Although the intermediate bivalent cobalt compound formed during the preparation of this material does not contain a peroxo group and is capable of absorbing oxygen, it did not appear to be worthy of study in view of the statement by Bucknall and Wardlaw that it is very unstable.

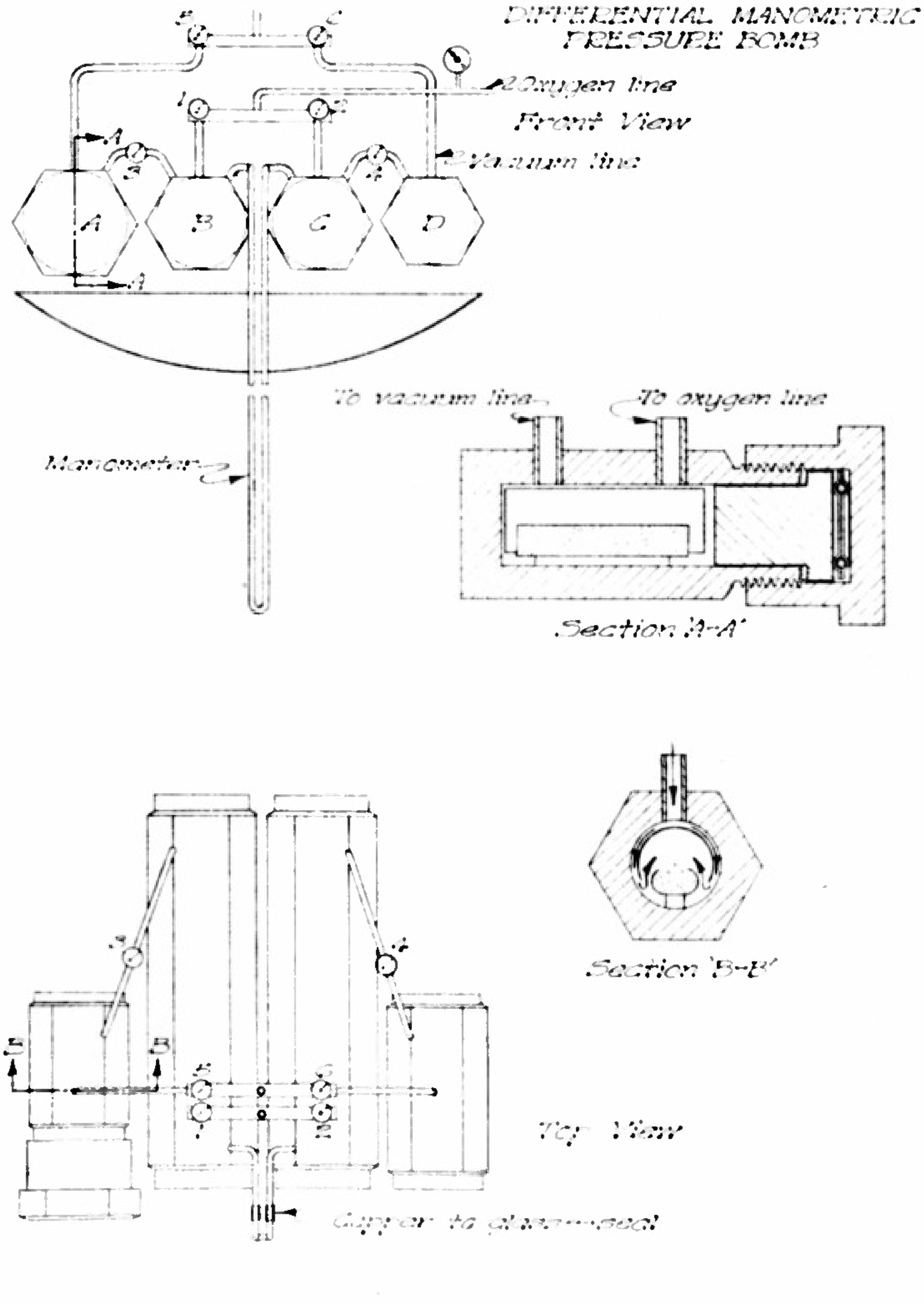
Although these results were not very encouraging, similar work should be repeated using triamines such as diethylenetriamine and 1,2,3-triaminopropane in place of allylamine.

X. Testing Apparatus

A. Apparatus for the Determination of Oxygen Capacity.

A differential manometric device to determine the oxygen-carrying capacity of compounds at various pressures and temperatures was constructed. This apparatus, shown in the accompanying diagram, consists of a row of 4 horizontal chambers suitably interconnected. The central chambers B and C are of equal volume of about 700 ml., the outer chambers, A and D, are of equal volume of about 75 ml. Chamber A is fitted with a screw cap which may be removed so that a sample of material to be tested may be placed in a chamber on a suitable boat. Chambers A and D are interconnected through valves 5 and 6 and may be evacuated through the pipe between valves 5 and 6. Chambers B and C are interconnected through valves 1 and 2 and may be charged with oxygen under pressure, the oxygen pressure

DIFFERENTIAL MANOMETRIC PRESSURE BOMB



being measured by a gauge on the oxygen line 6. The pressure in chambers B and C may be brought to the same pressure and chambers B and C then closed off from each other. The large chambers are also connected to the adjacent outer chambers through valves which may be opened to permit the oxygen to expand from the large chamber into the adjacent, small chamber. That is, the oxygen in B may be expanded through valve 3 into A, and the oxygen in C expanded through valve 4 into D. A differential manometer is connected between B and C. As the material contained in A absorbs oxygen, the pressure of the gas in A plus B falls below that in C plus D, and the pressure difference is recorded on the manometer. As will be seen from the mathematical development given below the actual pressure within the apparatus is not involved in the determination of the capacity of a material being tested.

The chambers of this apparatus are constructed of hexagonal, brass bushing of suitable size. The chambers are connected by means of 0.25 in. copper tubing. The valves were especially constructed of brass with stainless steel needles. The glass manometer was sealed to the copper tubing by a fused copper-glass seal. The screw cap of a chamber has a hexagonal head and is threaded about 20 threads to the inch. The collar which actually closes chamber A is backed up by a thrust ball bearing such that the collar does not turn when the screw cap is tightened. The entire apparatus is suspended rigidly from the wall. A well insulated box serving as a constant temperature bath, is mounted on a hydraulic jack such that it may be raised up about the apparatus. The box is equipped with a 0.25 H.P. refrigeration unit and has copper tubing wound around the inside walls. An alcohol-water mixture is placed in the box so that the apparatus can be operated at temperatures as low as -30°.

The sequence of manipulations in the operation of this instrument is as follows. A weighed sample of deoxygenated material contained on a boat is placed in chamber A and the sealing collar, gasket, and screw cap put in place and tightened. The entire apparatus is immersed in a bath and sufficient time allowed for the apparatus to assume the temperature of the bath. Valves 3 and 4 are closed. Valves 5 and 6 are opened, chambers A and D are evacuated and then valves 5 and 6 are closed. Valves 1 and 2 are opened, chambers D and C charged with oxygen to a pressure somewhat higher than the final pressure at which the capacity is to be determined, and valves 1 and 2 are then closed. Valves 3 and 4 are then opened simultaneously and carefully to avoid any pressure differential which might force the mercury of the differential manometer into chambers B or C. Sufficient time is allowed for the compound to be completely saturated with oxygen and the difference in the level of the mercury in the manometer is read. From this pressure difference, the weight of the sample, and the pressure difference of a blank determination, the capacity of the material is calculated using the following formula:

$$\text{Per Cent Oxygen Absorbed} = \frac{(100)\ 32}{W_s}\ \frac{(\Delta P_s - \Delta P_b)\ (V_{A+B} - \frac{W_s}{d})}{RT}$$

where

W_s	=	weight of sample
ΔP_s	=	pressure difference observed
ΔP_b	=	pressure difference observed during blank run
V_{A+B}	=	combined volume of chambers A and B
d	=	density of sample (taken as 1.5 for these compounds)
R	=	the Gas Constant
T	=	the absolute Temperature.

The formula was developed as follows, using the further definitions.

V_A, V_B, V_C, V_D	= volumes of chambers A, B, C, and D respectively.
V_{C+D}	= combined volume of chambers C and D
P_{A+B}	= pressure in chambers A and B when interconnected (valve 3 open)
P_{C+D}	= pressure in chambers C and D when interconnected (valve 4 open)
n_A, n_B, n_C, n_D	= number of moles of oxygen in A, B, C, and D respectively.
$n_A + n_B$	= number of moles of oxygen in A plus B when interconnected.
$n_C + n_D$	= number of moles of oxygen in C plus D when interconnected

At the beginning valves 3 and 4 are closed, 1 and 2 open and B and C charged with oxygen, and, valves 5 and 6 open and A and D evacuated. Valves 1, 2, 5, and 6 are then closed and the following conditions prevail:

$P_A = P_D$ (=1 mm. or less)

$P_B = P_C$ (5 psig up to 250 psig)

$P_A V_A = n_A RT$ and similar equation for B, C, and D

In a blank determination no compound is placed in A and the expansion is carried out. If the construction were perfect $V_A + V_B$ would equal $V_C + V_D$ and $P_{A+B} = P_{C+D}$. Since this is not actually the case, a slight pressure difference ΔP_b is obtained.

Applying the gas laws:

$$(1)\quad P_{A+B}(V_A + V_B) = (n_A + n_B)\,RT$$

$$(2)\quad P_{C+D}(V_C + V_D) = (n_C + n_D)\,RT$$

Subtracting (2) from (1)

$$(3)\quad \Delta P_b = P_{A+B} - P_{C+D} = \frac{(n_A + n_B)\,RT}{V_A + V_B} - \frac{(n_C + n_D)\,RT}{V_C + V_D}$$

When an oxygen absorbing material is present, let

n_a = moles of oxygen absorbed by compound

ΔP_a = observed pressure difference

then

$$(4)\quad P_{A+B}(V_A + V_B) = (n_A + n_B - n_a)\,RT$$

$$(5)\quad P_{C+D}(V_C + V_D) = (n_C + n_D)\,RT$$

and

$$(6)\quad \Delta P_a = P_{A+B} - P_{C+D} = \frac{(n_A + n_B - n_a)\,RT}{V_A + V_B} - \frac{(n_C + n_D)\,RT}{V_C + V_D}$$

$$(7)\quad \Delta P_a = \frac{(n_A + n_B)\,RT}{V_A + V_B} - \frac{(n_C + n_D)\,RT}{V_C + V_D} - \frac{n_a\,RT}{V_A + V_B}$$

introducing equation (3)

$$(8)\quad \Delta P_a = \Delta P_b + \frac{n_a\,RT}{V_A + V_B}$$

Owing to the variation of the diameter of the copper tubing the volume of chamber B is not exactly equal to the volume of chamber C and the volume of A not equal exactly to the volume of chamber D. Fortunately, this difference can be corrected without much difficulty as indicated in the above mathematical development.

As will be seen from the above mathematical analysis, it is necessary that the combined volume of chambers A and B must be known. This volume was determined by two different methods. In one method the volume of chambers A plus B was determined by expanding air from chambers A plus B into a flask of known volume, and measuring the change in the pressure of the system by means of the manometer. The flask was attached to the evacuation tube (between valves 5 and 6). Valves 1, 4 and 6 were closed and valves 2, 3 and 5 were opened. Thus, chambers A and B were connected to each other, to the flask of known volume, and to the manometer. The second arm of the manometer remained open to the atmosphere by way of chamber C, valve 2, and the oxygen line. The volume of the connecting tube between valve 5 and the flask was determined independently by a similar method and its volume subtracted in the determination of the volume of A plus B as just described. The volume of the flask itself was determined by weighing it full of water. The volume of chambers A plus B was found to be 779, 781, and 781 by 3 determinations. These values may be slightly in error because of the change in the volume of chambers A plus B as the position of the mercury in the manometer changes; this error has been determined to be less than 2 ml., and thus so small that it maybe neglected.

The volume of chambers A plus B was determined also by calibration of the apparatus against a sample of the parent, oxygen-carrying compound whose capacity had been very carefully determined by measuring the increase in weight on standing in pure, dry oxygen at atmospheric pressure (in this case saturation should not be made with high pressure oxygen because it was found that after complete saturation, the compound is still capable of absorbing a few tenths per cent of oxygen more, possibly by absorption). The results by this check the results of the first method within 2 ml.

This apparatus has made possible the determination of the oxygen-carrying capacity of the compounds studied at a variety of temperatures and pressures. With some compounds these determinations can not be made in the usual manner inasmuch as the compounds frequently, lose their oxygen spontaneously on being removed from an atmosphere of oxygen and can not therefore be weighed sufficiently rapidly to prevent error. Also some compounds are hygroscopic in nature and cannot be exposed for weighing.

This apparatus was also used for the determination of the rate of oxygenation in oxygen of certain compounds. See Part C below.

B. Apparatus for the Determination of the Rate of Deterioration.

Design and Construction of Rotating Drum Machine.

The primary objective of constructing this type of apparatus for the determination of the rate of deterioration of oxygen-carrying compounds was to minimize the temperature to which the material was heated during the deoxygenation step. In the stationary bed type of apparatus, deterioration may be accelerated by the fact that the material in immediate contact with walls of the heating jacket is necessarily heated to a higher temperature than it need be and thus remains in contact with oxygen at elevated temperatures longer than necessary. In the rotating drum machine, on the other hand, the mass of material is constantly mixed and is heated only to the temperature necessary to effect deoxygenation.

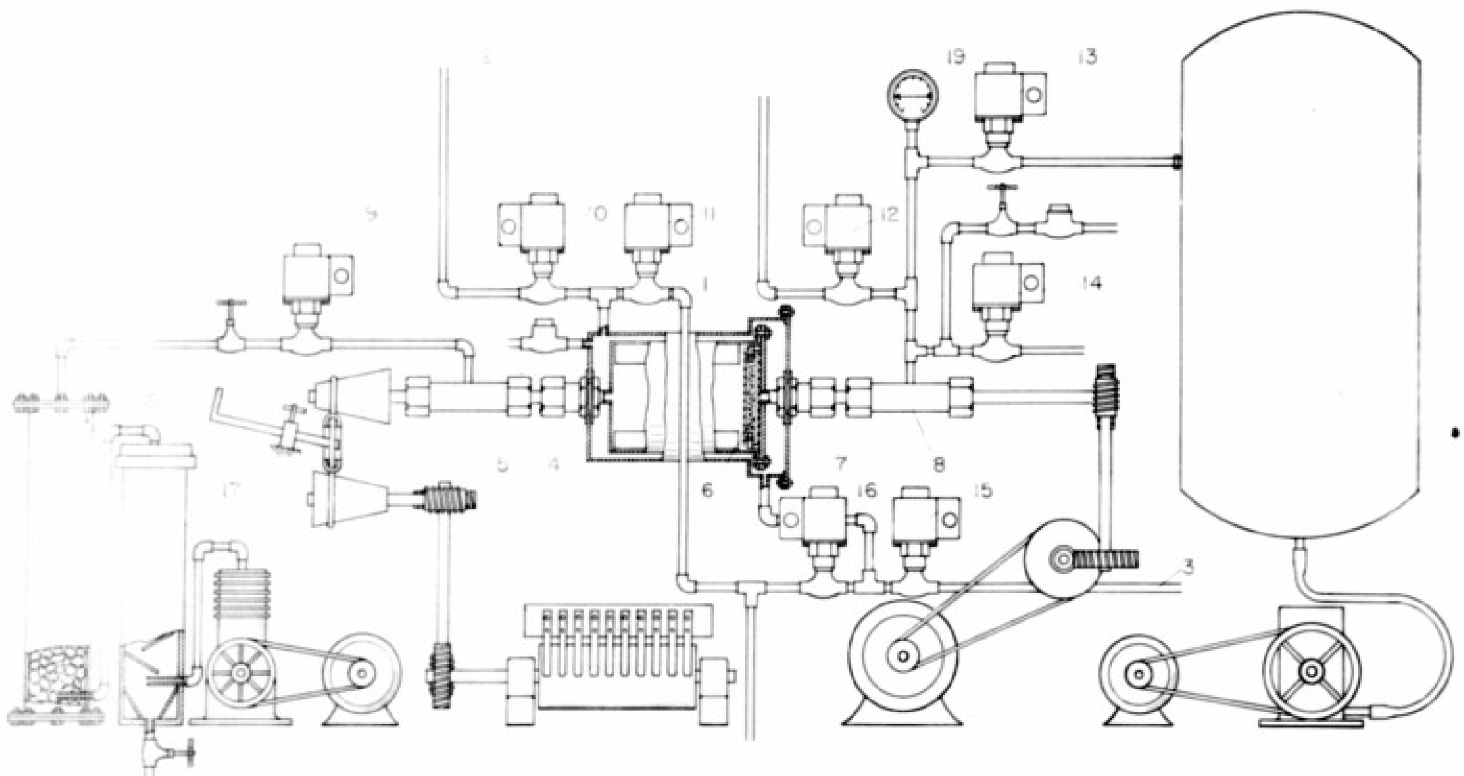
The apparatus designed for these tests is shown in the accompanying drawing. The apparatus consists of a drum (1) of about 0.2 cu. ft. capacity, which rotates within a jacket through which both steam (2) and water (3) may be passed. Air is passed into the drum containing the compound through a hollow shaft (4), the air entering the shaft through packing glands (5). The exit air passes through a filter (6) about 5 in. in diameter and then passes out through another hollow shaft (7) fitted with packing glands (8). The passage of the air through the drum and of the water and steam through the jacket is controlled by solenoid valves (9)-(16). The action of the valves is controlled by a cam with sliding electric contacts.

The air entering the machine passes through a trap (17) containing broken stone which is carried along mechanically in the air stream. The air then passes through a tower of walnut size potassium hydroxide and finally through a tower of magnesium perchlorate.

The exit air assembly consists of the hollow shaft (7), packing gland (8), pressure gauge (19) and three electric valves which control the outflow of air (bleed), vacuum (to exhaust the residual air before deoxygenation) and oxygen delivery.

The heating and cooling jacket is connected at the top to the steam line, at the bottom to the water line. These four outlets are equipped with electric valves. Both the steam and the water lines have manually operated throttle valves in addition to the solenoid valves.

The drive for the rotating drum and the cam consists of a 0.5 H.P. electric motor connected to the shaft on the rotating drum by means of a series of sprockets and roller chain,



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15
3

in such a manner that the drum turns with the speed of approximately 8 r.p.m. The timing cam is driven from the other end of the shaft by further sprockets, roller chain, and reduction gear; it turns at the rate of about one revolution every nineteen minutes.

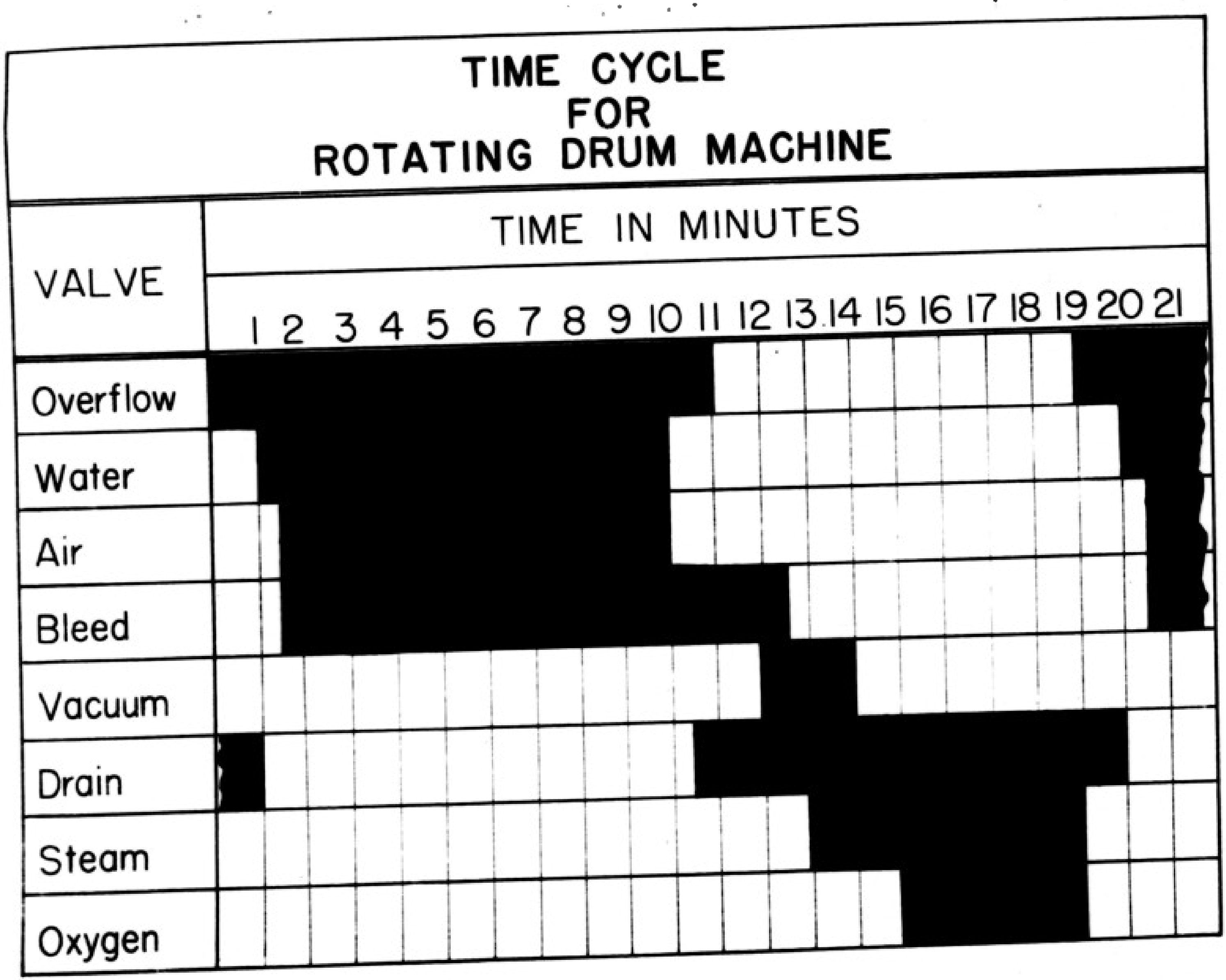
The accompanying diagram shows the machine in its first form. The drive and gear reduction mechanism of this machine has been modified, but the essential features of the machine are the same.

The sequence in the operation of this machine is given in the following description which can best be followed by means of the accompanying timing diagram.

1. The overflow valve on the heating and cooling jacket opens, connecting jacket to drain.
2. The water valve opens allowing water to pass into the heating and cooling jacket and to overflow into the drain.
3. The bleed valve on the exit air line opens. This valve is equipped with a hand operated valve so that the flow of the air through the compound can be controlled.
4. The air valve opens.
5. These valves remain open for approximately 10 minutes, during which time the material oxygenates.
6. The air and water valves close. The air in the drum escapes through the bleed valve and is reduced to atmospheric pressure.
7. The drain valve at the bottom of the jacket opens and overflow valve closes. The jacket is equipped with a check valve which allows the entrance of air permitting the water to drain from the jacket.
8. The bleed valve closes and the vacuum valve opens allowing the air in the drum to exhaust in the vacuum tank.
9. The steam valve then opens and the vacuum valve closes.
10. About one minute later, after the pressure in the tank has risen to nearly atmospheric because of the liberation of oxygen, the oxygen valve opens and oxygen is delivered.
11. After about seven minutes the steam, drain and oxygen valves close and the cycle is completed.

The cycle as the machine has been operated, is approximately 19 minutes in length. The operation is entirely automatic. It is only necessary to blow off the accumulated water in the mechanical water remover daily and to blow off the potassium hydroxide solution from the caustic drier every three days. Occasionally it is necessary to stop the operation of the machine, connect a nitrogen tank to the bleed valve, open the bleed valve, and blast nitrogen into the drum to remove the powder accumulated on the filter.

Two studies of the rate of deterioration of the parent oxygen-carrying compound and one of the 3-methoxy compound were made using this apparatus. The tests on the parent compound


TIME CYCLE
FOR
ROTATING DRUM MACHINE
VALVE
TIME IN MINUTES
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Overflow
Water
Air
Bleed
Vacuum
Drain
Steam
Oxygen

did not yield all of the data which was later desired concerning the rate of deterioration but did indicate some precautions which should be observed in the operation of machines using this material.

The first study indicated very rapid initial deterioration; this was undoubtedly due to the excessive rate of air flow used, about 1 cu. ft. per minute, about a 600 per cent excess. At 300 cycles, the air flow was reduced to 0.3 cu. ft. per minute, an excess of about 100 per cent; the rate of deterioration was considerably less after this change. The air used in this study was dried over anhydrous calcium chloride and was used at 70 psig. The temperature of the cooling water was 15°C.

In the second study the air was dried over magnesium perchlorate, the other factors being left unchanged, an excess of 100 per cent of air being used. There was no significant change in the rate of deterioration as a result of this change.

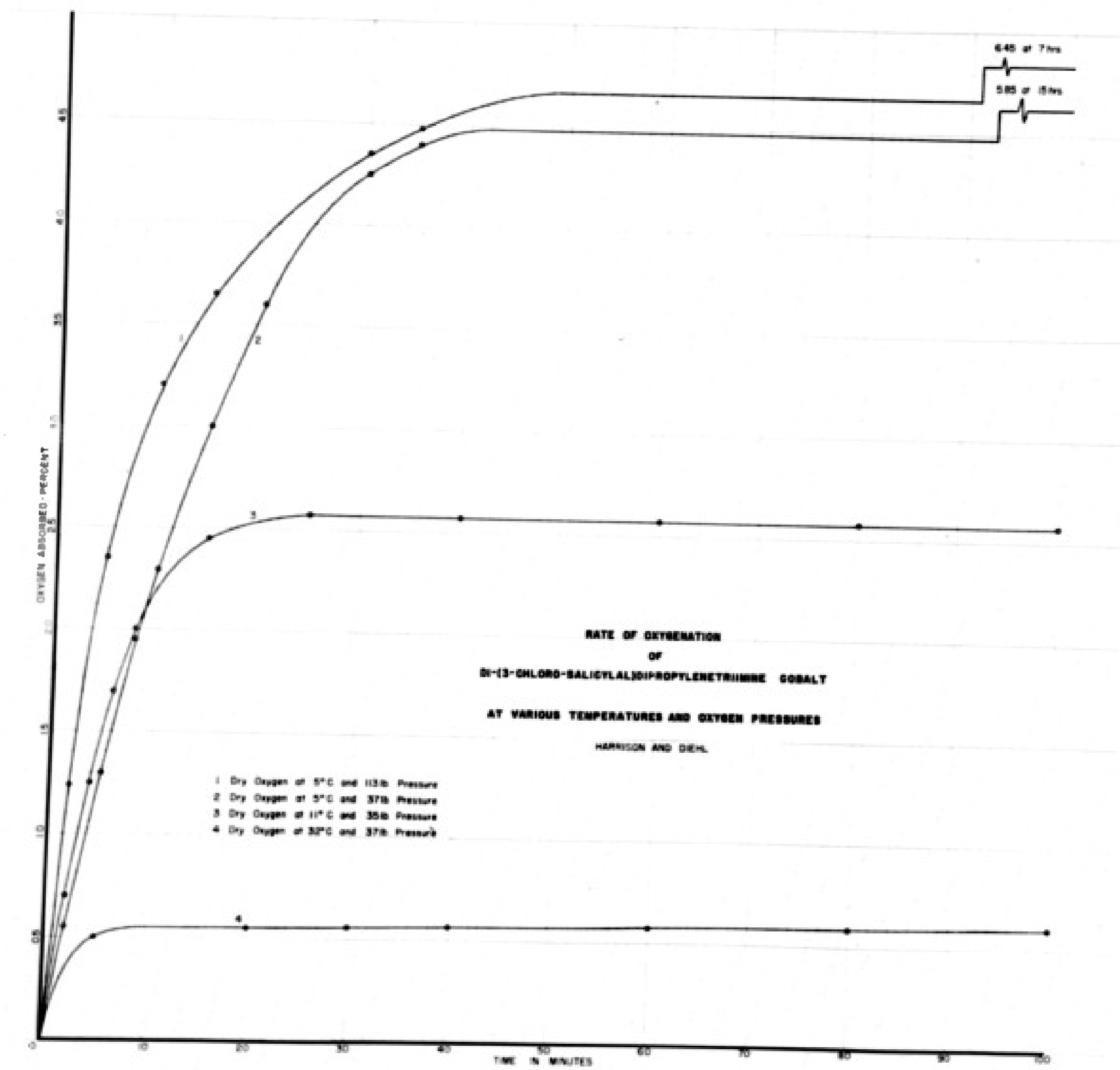
Unfortunately not all of the factors involved in the deterioration were appreciated when those studies were begun and the lack of data and the changes in conditions during the runs vitiate the significance. The conditions were better standardized in the study made on the 3-methoxy compound. This work will be found on p. 25 of this report.

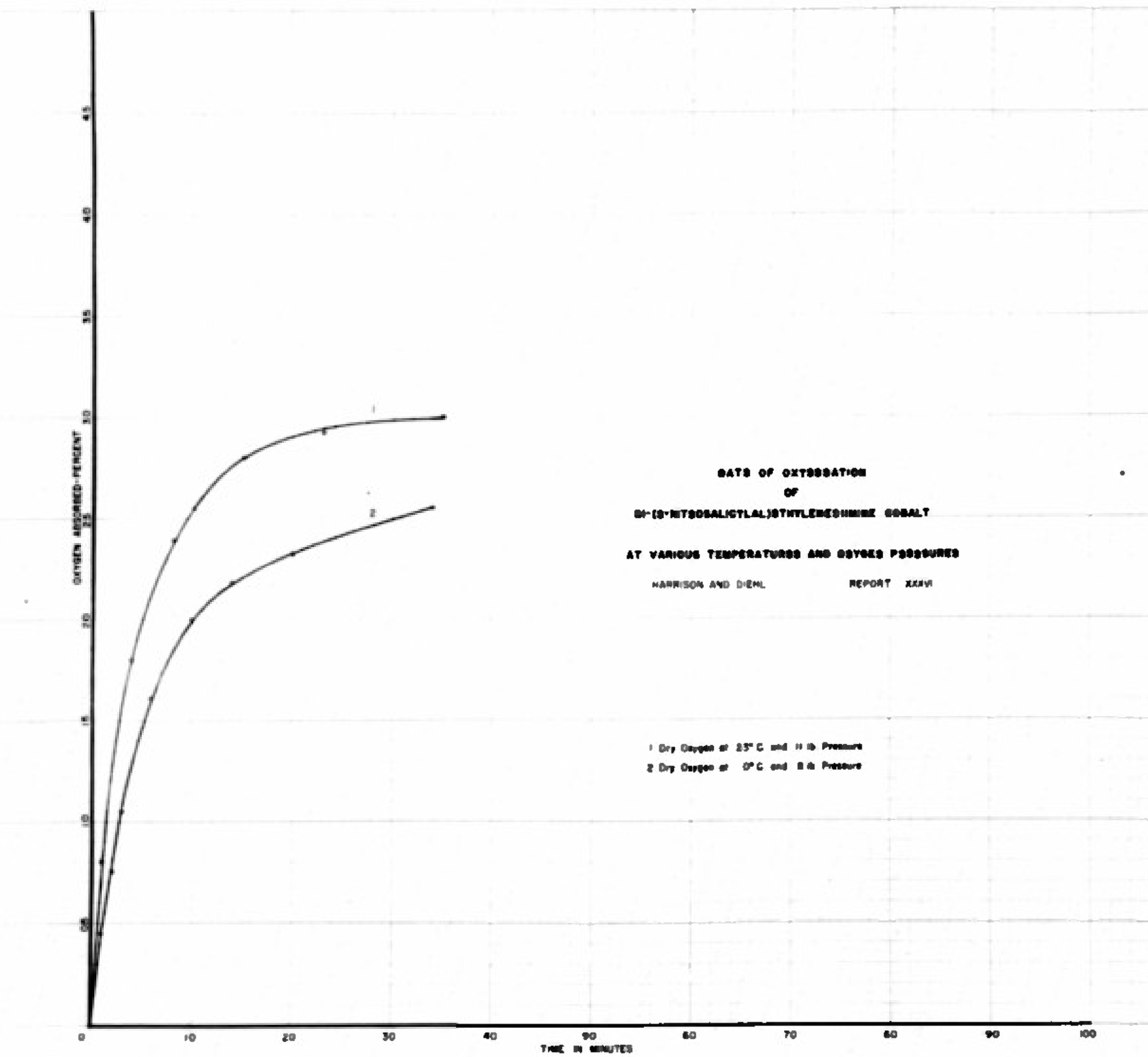
C. Apparatus for the Determination of the Rate of Oxygenation

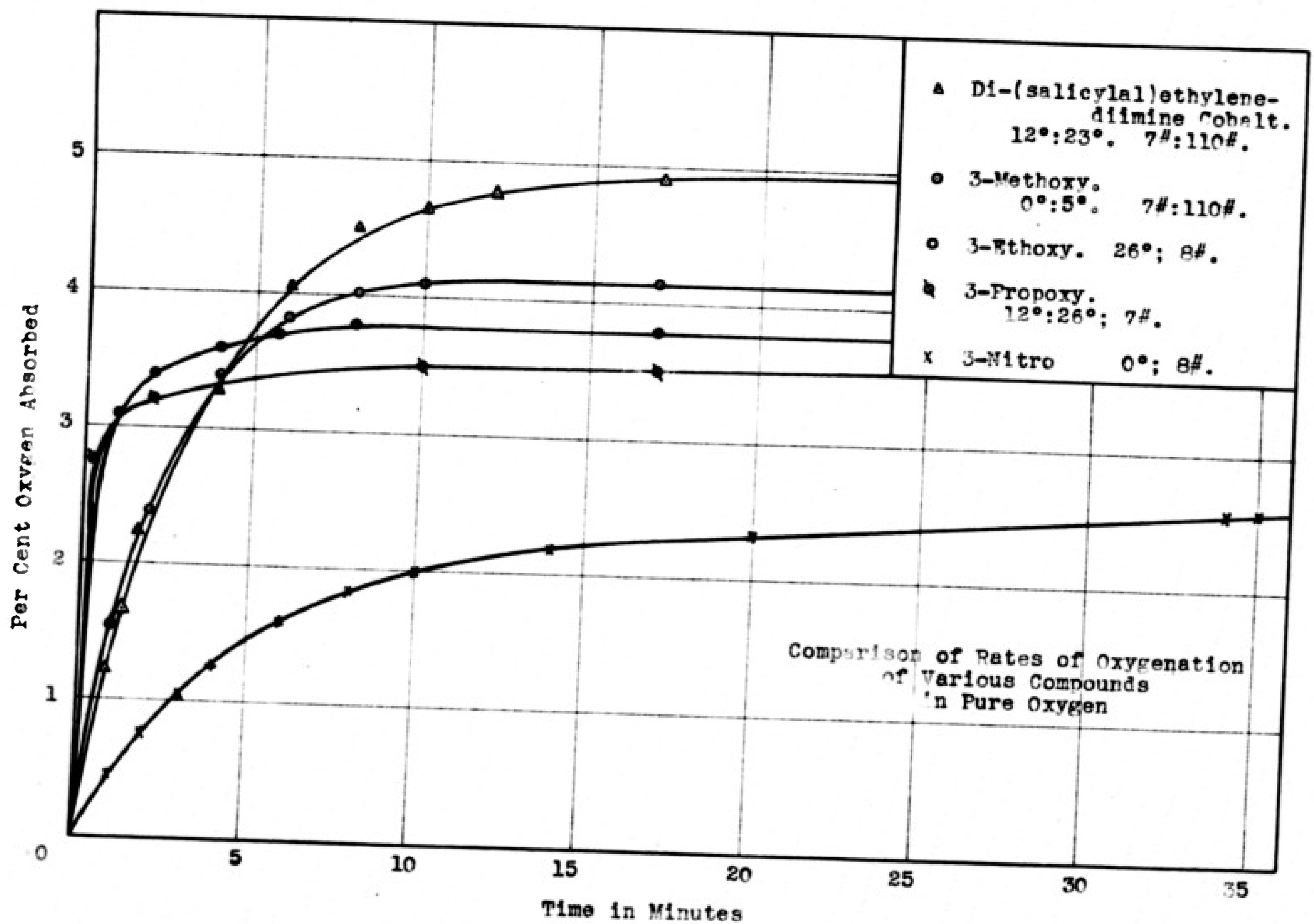
During the course of the development of this work, various methods have been used for determining the rate of oxygenation of the compounds under study. Preliminary data of the rate of oxygenation of new compounds is easily obtained by following the gain in weight of the compound on exposure to air on a watch glass on the balance pan. When the rate in dry air, in air at higher pressure, or in oxygen is desired a more elaborate method is required. For measurements of the rate of oxygen at pressure from 150 to 1500 mm. and temperatures from -20° to 100° the apparatus described by Hadh, Harrison and Diehl, Report III, is probably the best yet described. In this apparatus the material was placed in thin layers on fins which quickly conducted away the heat of reaction, and the rates obtained are probably as nearly isothermal as have yet been reported. The general method of determining the amount of oxygen absorbed by direct volumetric measurement of the gas absorbed, cannot be used with air since the latter must be circulated past the compound lest the oxygenation be stopped by the accumulation of nitrogen around the compound. Two apparatus for determining the rate in air are described below in (subsections (1) and (3)). The first involving the measurement of the increase in weight of the material on oxygenation and the second the decrease in pressure of a large volume of air in contact with a relatively small amount of material.

The method of determining the rate in oxygen described in subsection (2) is essentially a very simplified modification of the earlier apparatus of Hach, Harrison and Diehl and has been used to obtain rougher measurements with oxygen containing various amount of moisture. The differential manometric device described above in Part A for the measurement of the oxygen-carrying capacity of the compounds has been used for measuring the rate of oxygenation in pure oxygen. Although the chambers of the apparatus are of brass and the boat carrying the material of tin, it is not expected that the heat of oxygenation was carried away very rapidly. The rates obtained are therefore not strictly isothermal. They are, however, reproducible and indicative at least of the variation of rate with pressure. The rates of oxygenation of the parent compound and of di-(3-chlorosalicylal)dipropylenetriamine as determined in this manner are shown in the accompanying diagrams. The effect of temperature on the 3-chloro compound and also the final degree of saturation is readily apparent.

(1) Gravimetric Method. This method of determining the rate of oxygenation of an oxygen carrying compound was carried out in the following manner: A weighed sample of the compound to be tested was deoxygenated in a vacuum at 100°, and allowed to cool in a vacuum desiccator. The sample was transferred quantitatively to a clean, dry U-tube and the ends well packed with glass wool to prevent the loss of compound. The sample was again deoxygenated by placing the tube in a beaker of hot water and passing dry nitrogen through it. The tube was wiped dry and allowed to stand in the balance case to assume room temperature and then weighed using a similar U-tube as a tare. The weighed tube was then immersed in a beaker containing a liquid bath at the temperature at which the rate of oxygenation was desired and sufficient time allowed for the tube and contents to attain the temperature of the bath. The rate of oxygenation was determined by passing a stream of dry air through the tube for definite periods. The stopcocks were then closed, the tube wiped dry, brought to room temperature and weighed. The air was dried by passage through a tower filled with magnesium perchlorate. The most serious difficulty with this method is the inability to obtain an even and rapid flow of air through the tube since the oxygen-carrying compounds are powders which rapidly plug the glass wool packing. This difficulty was not encountered in the rate determinations reported for the methoxy compound, Section VI$_a$, Part B$_a$, subsection (8) of this report since this material was more crystalline in character.


RATE OF OXYGENATION
OF
DI-(3-CHLORO-SALICYLAL)DIPROPYLENETRIIMINE COBALT
AT VARIOUS TEMPERATURES AND OXYGEN PRESSURES
HARRISON AND DIEHL
1 Dry Oxygen at 5°C and 113lb Pressure
2 Dry Oxygen at 5°C and 37lb Pressure
3 Dry Oxygen at 11°C and 35lb Pressure
4 Dry Oxygen at 32°C and 37lb Pressure
645 at 7hrs
585 at 15hrs
OXYGEN ABSORBED-PERCENT
TIME IN MINUTES
0
10
20
30
40
50
60
70
80
90
100
05
10
15
25
35
40
45
1
2
3
4

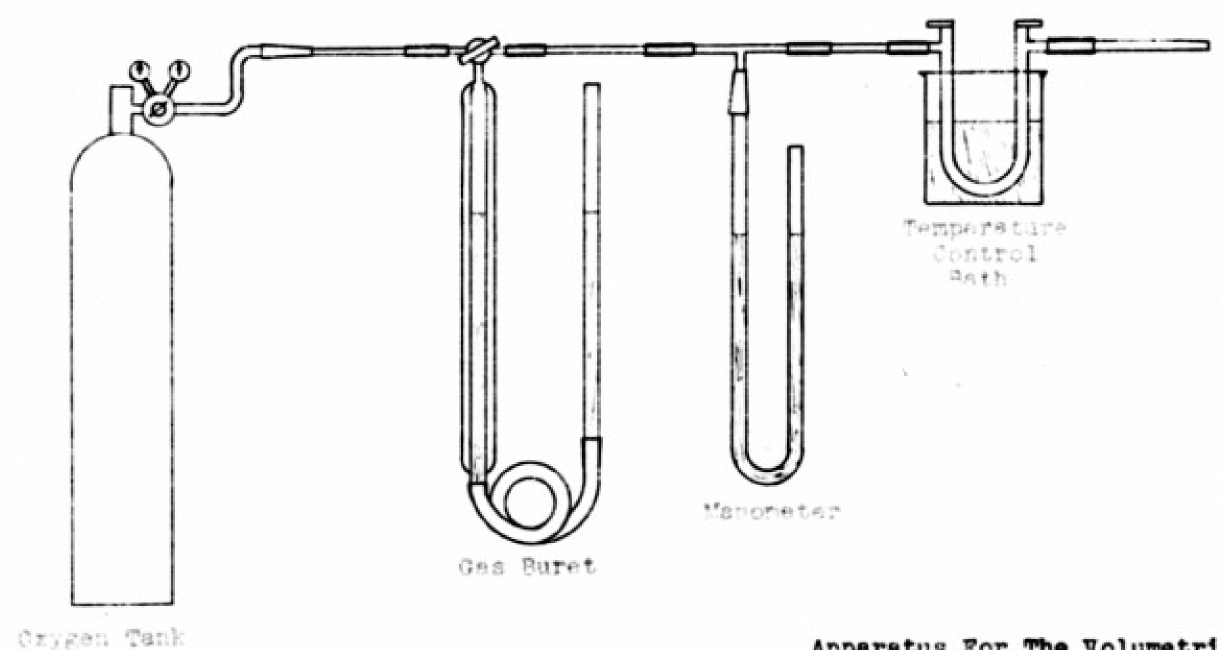

RATE OF OXYGENATION
OF
DI-(3-NITROSALICYLAL)ETHYLENEDIIMINE COBALT
AT VARIOUS TEMPERATURES AND OXYGEN PRESSURES
HARRISON AND DIEHL
REPORT XXXVI
1 Dry Oxygen at 25° C and 11 lb Pressure
2 Dry Oxygen at 0° C and 8 lb Pressure
OXYGEN ABSORBED-PERCENT
TIME IN MINUTES
0
10
20
30
40
50
60
70
80
90
100
05
10
15
20
25
30
35
40
45
1
2



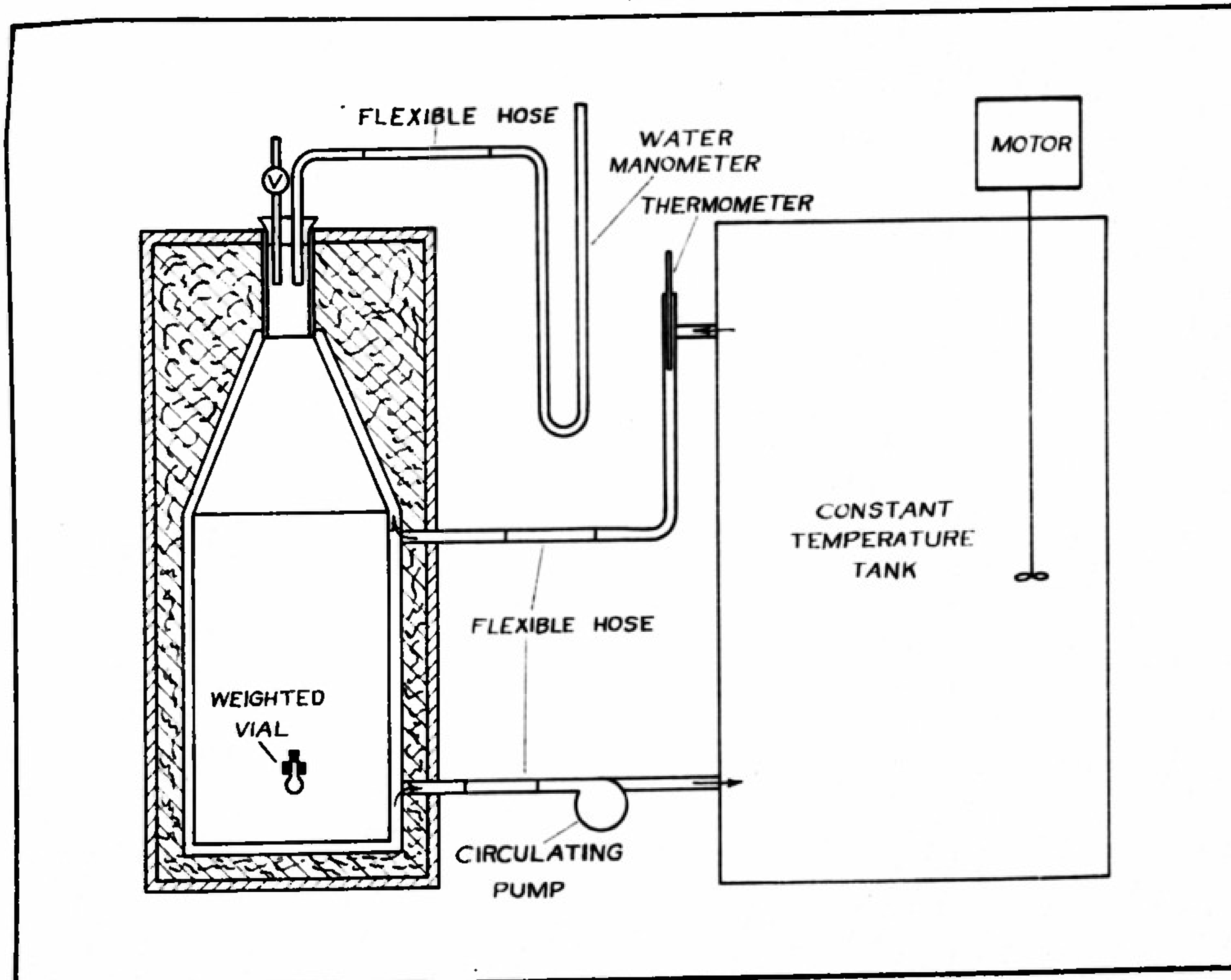
Di-(salicylal)ethylene-diimine Cobalt. 12°:23°. 7#:110#.
3-Methoxy. 0°:5°. 7#:110#.
3-Ethoxy. 26°; 8#.
3-Propoxy. 12°:26°; 7#.
3-Nitro 0°; 8#.
Comparison of Rates of Oxygenation of Various Compounds in Pure Oxygen
Per Cent Oxygen Absorbed
Time in Minutes
0
1
2
3
4
5
10
15
20
25
30
35

(2) Volumetric Method. The gravimetric method, described above in subsection (1), for determining the rate of oxygenation of the compounds under study was rather tedious to carry out and subject to certain disadvantages. The following volumetric method for determining the rate of oxygenation was also used although it could only be adapted to measuring the rate of oxygenation in pure oxygen. The apparatus is pictured in the accompanying drawing. The U-tube was filled with a weighed sample of the compound. The sample was then deoxygenated and activated by immersing the U-tube in a bath maintained at 120°. At the same time a stream of dry nitrogen was passed slowly through the U-tube to sweep out the oxygen and water. As soon as the deoxygenation and activation was complete, in approximately 15 minutes, the stop cocks on the U-tube were closed and the U-tube installed in the rate apparatus. Ample time was allowed for the compound to come to the temperature of the bath. Then the U-tube and tain up to the oxygen tank was evacuated. The buret was filled with oxygen from the cylinder. A salt solution was used as retaining liquid in the buret so as to give the oxygen contained in it the desired humidity. When the evacuation was complete, the vacuum pump was stopped and the stop cock on the U-tube was closed. Then the stop cock on the buret was turned in such a manner as to admit the oxygen to the U-tube. The leveling bulb was so handled that the pressure of the oxygen remained as desired through the run. Buret readings were taken at timed intervals and from the volume of oxygen absorbed and the weight of the sample, the weight per cent of oxygen absorbed was calculated.

(3) Manometric Method. Owing to the tediousness and packing troubles encountered in determining the rate of oxygenation of the various compounds in air using the gravimetric method described above, an apparatus was devised for measuring these rates which would overcome these difficulties. This method involves the measurement of the drop in pressure of an enclosed volume of air to which a sample of the oxygen-carrying material is exposed. The apparatus is shown in the accompanying plate. The apparatus consists of a well insulated, double walled container closed by a rubber stopper bearing a stop cock and tubing for connection to a manometer. The connections are made with flexible rubber tubing so that the container may be shaken. The manometer is an open arm, inclined, water manometer. The sample of the compound under investigation is weighed into a thin walled vial, the vial surrounded with a heavy lead collar, and the vial placed carefully in the container. Brine at the desired temperature is circulated through the jacket of the container. The double walled container is then evacuated and air at the desired humidity is admitted. The stopper is then placed on the container and the apparatus is allowed to stand for several minutes with the stop cock open, in order that the vial and its contents may come to the temperature of the



Apparatus For The Volumetric Determination of rates of Oxygenation


FLEXIBLE HOSE
WATER MANOMETER
THERMOMETER
MOTOR
CONSTANT TEMPERATURE TANK
FLEXIBLE HOSE
WEIGHTED VIAL
CIRCULATING PUMP

container. The stopcock is then closed and the apparatus allowed to stand several minutes more. If the manometer remains stationary, temperature equality of the jacket and contents may be assumed and the determination begun. The container is shaken vigorously to break the vial. Slow shaking is then continued in order to keep the sample in good contact with the air in the container. Pressure readings are taken on the inclined water manometer at timed intervals. Since the pressure of the air within the double walled container is affected by changes in temperature of the brine flowing through the jacket, it is necessary to determine the temperature changes of the brine during a run and to make corresponding pressure corrections. One degree temperature change of the brine will cause a 80 mm. change on the inclined water manometer if the latter is inclined at 25°. The temperature of the brine was determined to the nearest 0.05° by placing a thermometer graduated in tenths of a degree in the discharge brine line.

The weight per cent of oxygen absorbed by the sample is calculated from the pressure change in the container, the size of the sample, the volume of the container and the temperature change of the brine.

The container is quite large (6.5 liter) and the size of the sample quite small (3 g.) so that the change in oxygen pressure due to absorption of oxygen is small. Since the pressure drop in this apparatus is only approximately 3 inches in water, an inclined water manometer was used in order to secure sufficiently large manometer readings.

The apparatus was quite easy to operate and gave good results as evidenced by the fact that perfect agreement was found with two rate curves which were run on Co-Ox M by the weighing method.

XI. Circulating Solid Apparatus for the Manufacture of Oxygen.

A. Object and Advantages of Circulating Solid Apparatus

Among the various types of apparatus which may be used for the recovery of oxygen from the atmosphere by means of solid, oxygen-carrying materials, the type of apparatus in which the solid material circulates continously from the oxygenation portion of the apparatus to the deoxygenation portion and back is particularly intriguing. Such a circulating solid apparatus was described by Hach and Diehl, Report III, using the parent oxygen carrying compound, disalicylalethylenediimine cobalt. The oxygenation of disalicylalethylenediimine cobalt must be carried out with air at approximately 100 psi pressure in order that the oxygenation be effected in a reasonable length of time. The deoxygenation must, of course, be carried out at essentially atmospheric pressure in order to minimize the deterioration which might be unduely accelerated at elevated temperatures; it is also necessary to include an evacuation step or a flushing process at atmospheric pressure to remove the residual air left in contact with the oxygenated material. Thus, it is necessary to transfer the material from a relatively high pressure to a low pressure and back. The apparatus just referred to utilized a rather complicated "locking device" to effect this transfer, and, although the device worked, it was at this point that the circulating solid apparatus gave the most difficulty.

The discovery of di-(2-hydroxy-3-methoxybenzal)ethylenediimino cobalt, hereinafter designated as Co-Ox M, the development of which is described in section VI_2, part B_2 of this report, again directs attention to the circulating solid type of apparatus. The rate of oxygenation of Co-Ox M is approximately twenty times that of the parent compound. This greatly simplifies the construction of a circulating solid type of apparatus in that the locking device may be made much simpler.

Fundamentally, the circulating solid apparatus has certain advantages over batch type apparatus in which the bed of material is stationary or is tumbled or mixed. There is no mass of metal (tank or heating and cooling fins) which must be alternately heated and cooled, and thus there is a saving in the heat and cooling required and in the time that is taken to heat and cool the mass of metal. The stationary or mixing batch types of apparatus also require time for flushing or evacuating the residual air and as will be seen in the apparatus to be described, this flushing can be accomplished in the circulating solid machines without appreciable loss of time. The circulating solid apparatus affords a continuous delivery of oxygen and since the heating and cooling mechanisms operates continuously, they can be built smaller than in the apparatus where they function only a portion of the time.

The principal disadvantage of the circulating solid type of apparatus is the danger of explosion caused by sparks derived from contact of moving metal parts. In an atmosphere of oxygen, Co-Ox or Co-Ox M, can be caused to flash when ignited by a spark or red heat, and if enclosed such a flash can cause considerable damage. In any circulating solid apparatus this hazard must be considered and any possibility of producing sparks in the apparatus eliminated.

B. Description of the Apparatus.

(1) Mode of Operation. The essential characteristics of the circulating solid apparatus to be described are, first, that the oxygenation and the deoxygenation of the oxygen-carrying material are carried out in separate chambers, and second, that the deoxygenation is effected at a slightly higher pressure than the oxygenation. The Co-Ox M is first conveyed through the oxygenation chamber, where it is cooled and exposed to air, is then transferred to the deoxygenation chamber, where it is heated and where it releases its oxygen, and is then transferred back to the oxygenation chamber. This is shown schematically in Fig. 1 of the accompanying drawings.

The solid, oxygen-carrying material is moved by a system of screw conveyors which transfer the material continously around the system. The apparatus was designed to contain about 75 pounds of Co-Ox M, to circulate this material once every 15 minutes, and to generate a continous flow of about 100 cu ft. per hour of oxygen of 95 per cent purity.

An important part of this apparatus is the method by which the solid material is transferred from the oxygenation chamber to the deoxygenation chamber and back again without seriously contaminating the oxygen produced. This is accomplished by maintaining the connecting tubes completely full of the solid, oxygen-carrying material and maintaining the pressure in the deoxygenation chamber slightly above that in the oxygenation chamber. This causes a flow of oxygen through a porous, more or less compacted mass of the oxygen-carrying material which sweeps the air from the mass.


Oxygen discharge
Deoxygenation Chamber
Screw Conveyor in which air and oxygen are separated from each other.
Discharge Heating Medium
Screw Conveyor
Heating Medium
Screw Conveyor in which air and oxygen are separated from each other.
Oxygenation Chamber
Residual Gas Discharge
Discharge Cooling Medium
Cooling Medium
Air In

Fig. 1.

As will be seen from the curves given earlier in this report for the rate of oxygenation of Co-Ox M the optimum temperature for oxygenation of this material is about 5°. This means that mechanical refrigeration is required for cooling the oxygenation chamber. In order that the transferring devices mentioned work properly the deoxygenation must be effected at a slightly higher pressure than the atmospheric pressure at which the oxygenation is carried out; this requires a temperature of about 75°. Several schemes have been used to affect this heating and cooling.

(2) General Construction. As shown in Fig. 2 the oxygenation and deoxygenation chambers consist of two screw conveyors operating in pipes parallel to each other and inclined in opposite direction. These pipes are 9 in. in diameter and approximately 8 ft. long. They are connected to each other at each end (see Fig. 3) by pipes containing short screw conveyors. The flow of solid, oxygen-carrying material is indicated in Fig. 2 by arrows, the material moving up the inclined slopes of the oxygenation and deoxygenation chambers. The four screw conveyors are driven by a suitable system of reducing gears, sprockets, ring gears and chains as shown in detail in Figs. 2, 3 and 7. The rate of revolution of the screw conveyors may be varied from 4 to 100 r.p.m. Air enters the oxygenation chamber at its upper end, passes down through the chamber counter to the flow of Co-Ox M, and passes out through the large air filter shown. The oxygen liberated in the deoxygenation chamber passes through a large oxygen filter and out through the valve indicated.

The apparatus was originally designed to operate entirely on electric power. Difficulty, however, was experienced in obtaining suitable electric heating wire, and during the interim in which the heating wire was not available the apparatus was changed to operation by a gasoline engine from which heat could be obtained to effect the deoxygenation. The details of the power drive in each case are shown in Figs. 16 and 17. The gasoline engine used was a 6 H.P. Briggs and Stratton (Milwaukee) motor, equipped with a pulley clutch. When operated electrically a 0.5 H.P. motor was used to drive the conveyors. The oxygenation and deoxygenation chambers are provided with means by which they can be cooled and heated respectively. The entire apparatus is mounted on a wood platform and is suitably braced by steel supports.

The details of the oxygenation chamber are shown in Fig. 4. The oxygenation pipe and the jacket surrounding it are constructed of 18 ga. sheet steel with a welded seam. A brass bending is brazed on the screw conveyor over its entire edge,

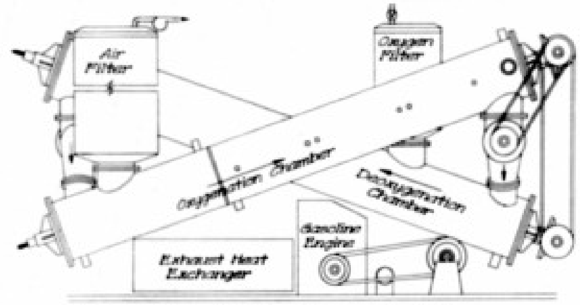


Fig. 2. Side View—Position of Respective Parts.
(Note: All flanged connections are gasketed and fastened by ⅜" cap screws)

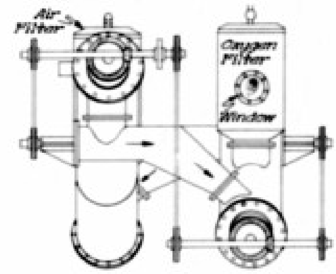


Fig. 3. End View—Cross Augers Connecting Oxygenation Chamber to the Deoxygenation Chamber

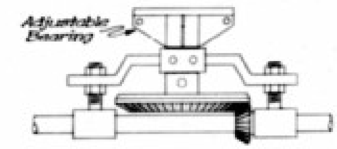


Fig. 8. Driving Mechanism for Long Augers

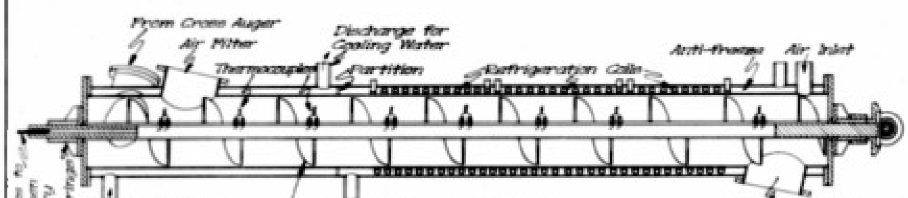


Fig. 4. Oxygenation Chamber

Brushes are attached the entire length of the auger edge in both Chambers.

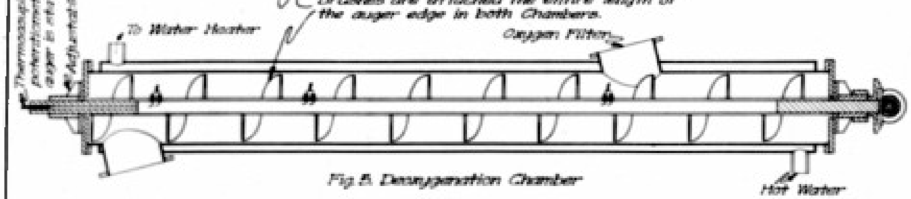


Fig. 5. Deoxygenation Chamber

Details of Filters

Fig. 9. Air Filter

Fig. 10. Oxygen Filter

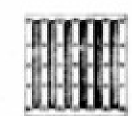


Fig. 11. Top View of Filters

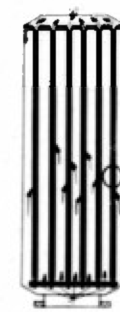


Fig. 12. Section 'A-A'

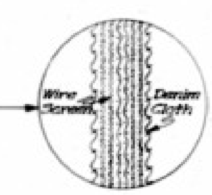


Fig. 13.

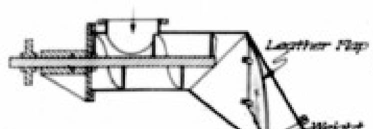


Fig. 6. Cross Auger First Model

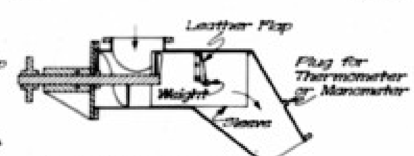


Fig. 7. Cross Auger Second Model

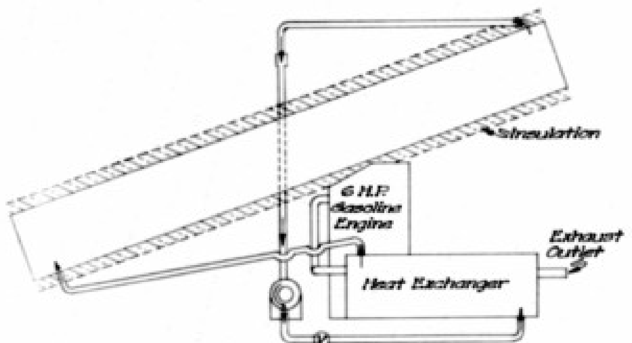


Fig. 14 Circulation of Hot Water in Deoxygenation Chamber Jacket. (Steam used as alternate, and Heat Exchanger and Pump eliminated from system.)

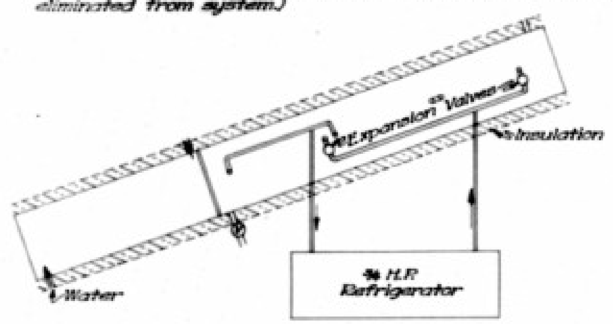


Fig. 15. Circulation of Refrigerant (Freon) Through Copper Coils Surrounding Oxygenation Chamber and Within Jacket. 50-50 Alcohol-Water Mixture in Jacket.

(Note: All water pipes and Heat Exchanger are insulated.)

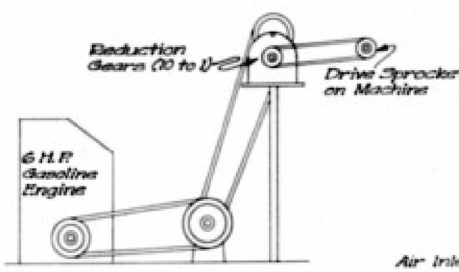


Fig. 16. Power Transmission to Machine From 6 H.P. Briggs & Stratton Gasoline Engine.

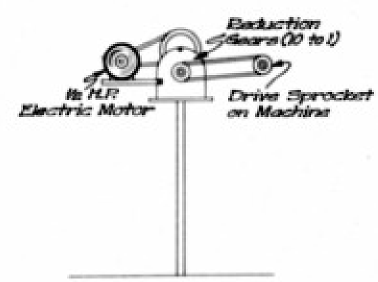


Fig. 17. Power Transmission to Machine From ½ H.P. Electric Motor.

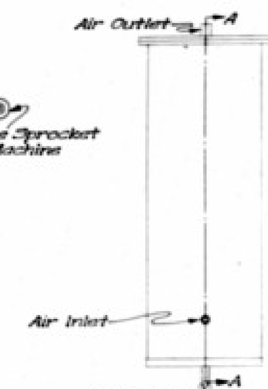


Fig. 18. Air Drying Chamber

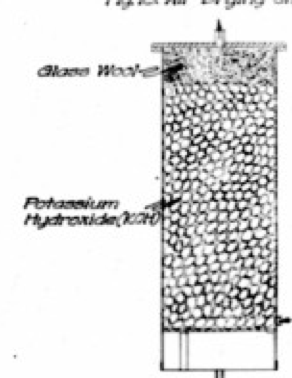


Fig. 19. Section "A-A"

where it might possibly come in contact with the steel pipe. Eight thermocouples, placed at intervals, are carried on the conveyor; the leads project out the lower end of the hollow conveyor shaft, and may be connected to a potentiometer when the apparatus is stopped. A narrow plate is welded between every other flight of the conveyor in such a manner as to assist in mixing the material as it moves along. The jacket surrounding the oxygenation chamber is divided into two portions. The upper jacket contains three sets of 0.5 in. copper coils through which a refrigerant is passed. The jacket is surrounded by a 2 in. layer of rock wool insulation.

The deoxygenation chamber, shown in detail in Fig. 6, likewise consists of a steel pipe of 18 ga. sheet steel with welded seam. It is surrounded by a jacket through which steam or hot water may be passed. The conveyor carries three thermocouples and mixing blades. This jacket is also insulated.

Direct contact of the conveyors with the pipe is avoided and to insure motion of the material a brush prepared by twisting looped binder twine in baling wire is attached to the outer edge of the conveyors over their entire length.

The various components of the apparatus are joined together by means of numerous flanges so placed that the component parts of the apparatus can be readily dismantled.

Open arm manometers are placed at each end of the oxygenation and deoxygenation chambers to indicate the pressure within the apparatus at various points.

(a) Air Filters. To effect the oxygenation of 75 pounds of Co-Ox M during a 15 minute interval requires a quantity of air of about 15 cu. ft. per minute, allowing about 2.5 times the theoretical amount of air required. From previous experiences it was known that a filter of very large area would be required to thoroughly remove the fine, dusty, oxygen-carrying material from the air stream. It was also known that the conductivity of the filter decreased as the filter became caked with the material. Experiments, however, indicated that there was a saturation point beyond which the conductivity of the filter no longer decreased with increase in the thickness of the cake on the filter. The filter for the air stream was designed to have a filtering area of about 30 sq. ft., a value which seemed large enough so that the required capacity would be maintained regardless of the amount of cake on the filter cloth. The filter on the oxygen stream was made smaller as it needed a capacity of only 2 cu. ft. per minute. Details of these filters are shown in Figs. 9, 10, 11, 12, and 13. The filters are made of a very tightly woven cloth (ticking) supported by a suitable arrangement of wire cloth and screen.

As stated before, it is essential for the operation of the apparatus that the pressure in the deoxygenation chamber be slightly higher than that in the oxygenation chamber. This pressure difference controls the purity of the oxygen produced and the loss of oxygen through the cross augers. In order to maintain an absolutely constant pressure in the oxygenation chamber, even though the conductivity of the residual gas discharge filter changes with time, the air is exhausted from the residual gas filter instead of being forced into the oxygenation chamber by a blower. Thus, the pressure in the oxygenation chamber is always at approximately atmospheric pressure. Experience, however, later indicated that the change in pressure drop across the filter was insignificant and that it is equally satisfactory to blow the air through the apparatus. The pressure in the deoxygenation chamber is controlled by a throttle valve in the oxygen discharge line.

(b) Heating and Cooling. As stated before the apparatus was initially designed to operate entirely electrically, and it was proposed to heat the deoxygenation chamber by electric heating wire (250 ft. No. 8 B. S. gauge Chromel wire, operating on 220 volts, supported on steatite fish-spine insulators) wound around the chamber. Because of the delay encountered in securing this wire, a jacket was placed around the deoxygenation chamber so that steam could be passed through it. It also appeared possible to make the apparatus entirely self-contained by operating the apparatus by a gasoline engine and it appeared possible also to secure the required heat by utilizing the exhaust gases from the engine. A heat exchanger and water circulating pump were placed on the apparatus. It was found however that there was not sufficient heat in the exhaust from the engine to heat the water required, about ten gallons, above 60°C. It was felt that there was sufficient heat carried away by the cooling air passing over the head of the Briggs and Stratton engine to have been sufficient to supply all of the heat required. It might be possible, therefore, to secure all of the heat necessary by using a water cooled engine and circulating the radiator water through a heat exchanger to secure further heat from the exhaust gases and to then circulate it through the jacket about the deoxygenation chamber.

Experiments with wheat flour indicated that with steam passing through the jacket there was sufficient heat transfer to elevate the temperature of the flour from 5° at the inlet end to 70° at the outlet end.

In order that the Co-Ox M oxygenate in a sufficiently short period of time, its temperature must be reduced to 5°, the optimum temperature of oxygenation. This is lower than can be obtained with ordinary cooling water and therefore refrigeration becomes necessary. It appeared more economical at first, however, to use cooling water to remove a large portion of the heat and to complete the cooling by refrigeration. The jacket surrounding the oxygenation chamber was therefore constructed in two sections. Through the lower section cooling water was passed. A total of 150 ft. of 0.5 in. copper tubing, in three equal sections was wound around the oxygenation pipe within the upper section of the jacket. This copper tubing was wound in three units so that the refrigeration liquid could be expanded in each. The jacket was filled with a 50-50 mixture of water and alcohol. Experiments with wheat flour indicated that flour entering the oxygenation chamber at 70° was cooled during its passage through the chamber to about 5° if the flour remained dry and moved freely along the tube. During the early experiments leaks frequently developed in the apparatus and the flour became wet and coated the chamber preventing adequate heat transfer. It is therefore essential that the apparatus be operated dry. This must absolutely be the case when Co-Ox M is used since it is rendered inactive by moisture.

The refrigerator used was a 0.75 H.P unit containing Freon-12 as the refrigerating liquid. The temperature of the alcohol mixture in the jacket was reduced to -25° when the apparatus was stationary, and rose to -15° when the apparatus was in operation.

(c) Transferring Device. The transfer of Co-Ox M from the oxygenation to the deoxygenation chamber must, of course, be made with the minimum carry-over of air. The temperatures prevailing in the oxygenation and deoxygenation chambers are such that deoxygenation is effected at a slightly higher pressure than the oxygenation. A stream of oxygen, therefore, always flows out of the oxygenation chamber and use is made of this oxygen to flush away the air carried with the Co-Ox M as it is transferred to the deoxygenation chamber and to prevent air from entering the deoxygenation chamber when the material is transferred from the deoxygenation chamber to the oxygenation chamber. Details of two models of these transferring devices or cross augers are shown in Figs. 6 and 7. The first model, shown in Fig. 6, was not entirely satisfactory. It consisted of the horizontal auger and an inclined tube as shown. A leather flap was placed in the inclined tube to retard the flow of Co-Ox M. Thus the pipe was completely enclosed by the leather flap and the cake of solid material beneath the flap. A small amount of oxygen flowed from the deoyxgenation chamber through the cake of solid material into the oxygenation chamber. The design shown in Fig. 7 was very satisfactory. The screw conveyor was made considerably shorter and the auger pipe lengthened by the insertion of a sleeve. A leather flap, smaller than that in the first model, was placed about midway between the end of the auger and the discharge end of the sleeve. A cylinder of solid material was passed beneath the flap and out the discharge end of the sleeve, from which it fell, into the oxygenation or deoxygenation chamber, respectively. This device was found to be free of any tendency to plug.

The efficiency of this transferring device was tested using wheat flour to imitate Co-Ox M. A test was made to determine the combined loss through the closed augers as a function of the difference in pressure between the oxygenation and deoxygenation chambers. A gas holder was filled with oxygen and was connected to the deoxygenation chamber. The pressure in the system was regulated to a desired value, the conveyors were driven, moving the flour through the machine, and the losses were observed by the lowering of the calibrated gas holder. Successive runs were made with oxygen pressures from 1.5-6 in. of water pressure. The results are given in Fig. 20. A second test was made to determine the amount of air carried into the deoxygenation chamber with the flour as a function of the pressure differences between the deoxygenation and oxygenation chambers. A measured flow of oxygen was passed through the deoxygenation chamber while the machine was running. When equilibrium conditions had been reached, a sample of the discharge oxygen was taken and analyzed. From the rate of flow and the composition of the discharge gas the amount of air carried with the flour into the deoxygenation chamber was determined. A series of runs were made with pressure differences between the deoxygenation and oxygenation chambers from 1.5-6 in. of water pressure. The results are plotted in Fig. 21.

Assuming that the machine was producing 150 cu. ft. of oxygen per hour, estimates were made of the purity of the oxygen to be produced as a function of the difference in pressure between the oxygenation and deoxygenation chambers.

Table 1. Oxygen Purity Estimates
(Assuming 150 cu. ft./hr. production)

Difference in Pressure	Purity	Loss through Cross Augers
6 in. water	99.4 per cent	10 per cent
4	99.2	8
2	99.0	4
1	98.9	2

Although the characteristics of wheat flour are not exactly those of Co-Ox M it was felt that these calculations were a reliable guide to the performance of the apparatus. As will be seen later this was justified.

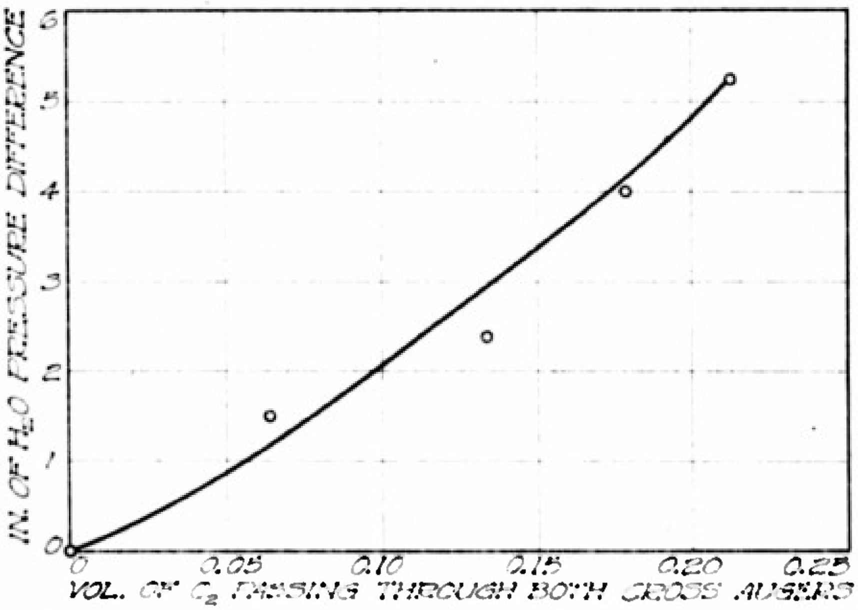


Fig. 20. Volume of O_2 passing through cross augers Vs. pressure.

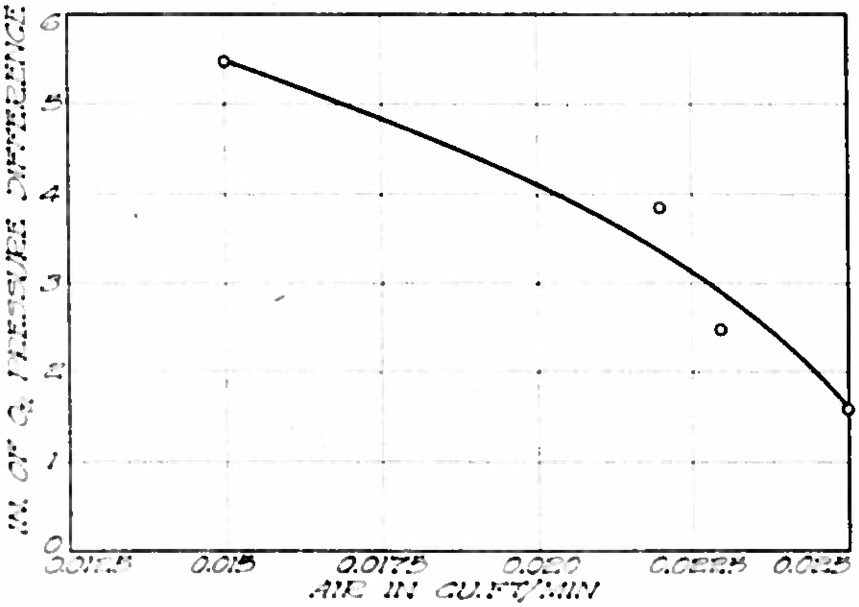


Fig. 21. Quantity of air carried with flour through cross augers Vs. O_2 pressure.

(d) Air Drier. The air entering the apparatus passes through a tower of walnut size potassium hydroxide. The details of this drier are shown in Fig. 18 and 19. The tower consists of a steel drum 5 ft. in height and 18 inches in diameter. The potassium hydroxide is supported on a perforated iron plate and is covered by a layer of glass wool which filters out any potassium hydroxide which might be carried by the air stream. Following the potassium hydroxide tower is a second tower consisting of a steel drum 3 feet high and 12 inches in diameter, charged with anhydrous magnesium perchlorate.

This combination and quantity of potassium hydroxide and magnesium perchlorate is sufficient for drying approximately 20 cu. ft. of air per minute to an extent which is satisfactory even with such a hygroscopic material as Co-Ox M.

(3) Operation and Modifications of Original Design. The apparatus was first placed in operation July 13, 1942. Prior to loading the apparatus with Co-Ox M, dry air was sucked through the apparatus to sweep out moisture. The compound was then introduced by removing the oxygen filter and feeding in the solid as the conveyors rotated. After sufficient time for the solid to have made a complete circuit through the apparatus, no oxygen had been produced. On inspection it was found that the first third of the material which had passed through the apparatus had turned yellow indicating that the material had absorbed water. This water was assumed to have come from condensation on the inner wall of the oxygenation chamber, this chamber having been cooled by refrigeration before sweeping the apparatus with dry air. This hydrated material was removed and operation carried on with the remainder. Oxygen was produced, though only at the rate of about 5 cu. ft. per hour. Several leaks were detected and the apparatus was shut down and emptied so that the entire mass of material could be reactivated and the necessary changes in the apparatus made.

In the second operation, 98 pounds of Co-Ox M was placed in the apparatus. Steam at atmospheric pressure was used for heating and the conveyor was driven by electric power. Dry air was swept through the apparatus for 1.5 hours before the refrigerator was started and the compound introduced. The apparatus delivered 12 cu. ft. of oxygen per hour of purity of 88 per cent after 30 minutes operation, 92 per cent after 45 minutes, and 93.5 after 1.5 hours. The pressure drop over the potassium hydroxide drying tower amounted to about 0.5 in. of water (the magnesium perchlorate drier had not been added at this time) so that the oxygenation chamber operated under a very slight vacuum. A slight further pressure drop occurred over the oxygenation chamber itself, the pressure just below the air filter being about 1 in. of water less than atmospheric pressure. The pressure at the discharge end of the oxygenation chamber (where the air entered) varied from 0.5 to 1 in. depending on how much material the conveyor was discharging. The pressure in the deoxygenation chamber was maintained at about 1 in. above atmospheric by regulating the valve on the oxygen discharge line; this required no attention after once adjusted.

The purity of the oxygen produced is governed by the difference in the pressures in the two chambers. The results indicated that the cross auger device worked even better than planned. It was calculated that if 100 cu. ft. per hr. of oxygen were being generated the purity of the oxygen would exceed 99 per cent, since the quantity of air carried into the deoxygenation chamber is constant and independent of the other factors which were affecting the amount of oxygen produced.

The temperature of the material leaving the deoxygenation chamber was measured by a thermometer inserted in the discharge pipe beneath the end of the conveyor. The temperature of the material varied from 65-75° depending on where the thermometer was placed in the cross section of the pipe. The material thus appeared to be adequately heated for deoxygenation.

The temperature of the material leaving the oxygenation chamber was similarly measured and found to be 35°. The cooling thus appeared to be very inadequate. The cooling arrangement was modified by eliminating the cooling water and by means of a pump circulating the 50-50 water-alcohol brine through both parts of the jacket, that is over the copper refrigerating coils, through the lower part of the jacket and back. This lowered the outlet temperature to 30°C. The rate of transfer of solid material was then decreased by reducing the conveyor speed from 10 to 5.5 r.p.m. This lowered the outlet temperature to 24°. The temperature of the brine was -6° indicating a temperature differential between the discharged material and the brine of about 30°. This is about that of the deoxygenation chamber.

The amount of heat extracted by the refrigerator was calculated from the pressures on each side of the compressor and the characteristics of the compressor. The performance coefficient of the refrigerator was calculated to be 3.7, indicating that it was greatly overloaded and not functioning as efficiently as possible. About 6040 B.T.U. per hour were being extracted. The amount of heat which must be removed was calculated to be about 21,000 B.T.U. per hour. It appeared, therefore, that the refrigerator alone was far from sufficient to effect the necessary cooling. Since the water cooling did not appear to contribute much, it appeared best to not use it at all and to use a larger mechanical refrigeration unit.

A 5 H. P. refrigeretion unit wes obtained and the expanaion of the refrigerant from this unit carried out in 400 ft. of 0.5 in. copper tubing arranged in 4 perellel linea of 100 ft. each. Thoae ooile were immersed in a 50-50 water-alcohol brine contained in a large insulated oil drum. The brine was circuleted from the oil drum through the jooket of the oxygenation chamber by means of a centrifioal pump. Tha 1 H.P. refrigeretion unit opereting the coila within the oxygenation chamber wee elso operated. With all of this refrigeration the temperature of the brine was lowered to a -15°, but the materiel leaving the oxygenation chamber was cooled only to 24°. The output of the machine increased to 15 cu. ft. per hour. Obvioualy, even with a 35° temperature differential the heat wes not being properly extracted from the material during oxygenation.

Some speculetions were mede as to the importance of precooling the entering air, and although the emount of heat oarried by air is small it wes thought worth trying. A finned, air cooled refrigeration condenser approximately 4 ft. by 2.5 ft. in cross seotion and 1 in. thiok was obtained and the pipes in it connected to e 0.75 h.p. refrigeration unit. A ply wood box wae built about this finned condenaer in such a manner thet the eir pasaed back and forth through the condenser. The air leeving this cooling unit was cooled to a -15°. This precooling increased the oxygen output of the apparatus about 5 cu. ft. per hour.

The inability to transfer heet from the material during the oxygenation prompted e number of measurements on the rete of heat tranafer of the material. As a result of these studies it appeared that there was aufficient surface in the oxygenation chamber to effect ell of the neceasery heat transfer at the temperature differential obtained. Since such transfer however wae not ectually being accomplished, it wes assumed that the mixing wae inadequate during the conveyanoe of the materiel through the chamber. The ecrew conveyors of both the oxygenation and deoxygenation chamber were then modified and their speed of rotation increased from 5 to 60 r.p.m. The brushes which hed been placed along the edges of the flights of the screw conveyor were removed and hinged, beveled meple strips such es are found on the dashere of ice cream freezers were placed between the flights in diametrically opposed positions. A sufficient number of beck paddles were placed on the flights of the conveyors with the object of decreasing the effectiveness of the conveyors end thus maintain epproximately the same flow of material through tha chambers as tested with flour. Pronge were elso added at various points to the conveyor to give a mixing and churning effect to the material. With these modifications the heet transfer in the deoxygenation chamber wes greatly improved, the materiel being raised from 20° et the inlet end to 101° at the outlet end, e temperature within 4° of that of the steam in the jacket of the deoxygenation chamber. On the other hand not much improvement was found in the oxygenation chamber, the material being cooled from 101° at the inlet end to 20° at the outlet end. The production of oxygen was about 25 cu. ft. per hour and was extremely steady. The oxygen output had previously been rather erratic tending to vary considerably, probably due to an uneven distribution of the material in the screw conveyors. The better mixing and more rapid rotation of the conveyors resulted in a more uniform flow of material. The failure to cool the material sufficiently in the oxygenation chamber was then attributed to a possible insulating effect of a wall film of the air which passes through the oxygenation chamber but is absent in the deoxygenation chamber. To test this effect, an atmosphere of oxygen supplied from a cylinder was placed in the oxygenation chamber and a very slight flow of oxygen maintained through the chamber during the operation of the apparatus. This increased the output of oxygen to about 30 cu. ft. per hour. The temperature of the material leaving the oxygenation chamber rose to about 25°. It appeared therefore that oxygenation was taking place to a greater extent and that the correspondingly great amount of heat rapidly raised the temperature of the material; the insulating effect of the moving air film was negligible.

The remaining explanation for this surprising difference in heat transfer is that the material when hot acts more as a fluid and flows and churns more easily than the material which is cold and inclined to mat and form masses which are not easily deformed. The deoxygenated material does flow like Portland cement while the black oxygenated material does not behave in this manner but tends to pack and move more like wet sand.

In these experiments no measure was actually made of the rate at which Co-Ox M was being transferred through the apparatus. Such measurements were made on wheat flour and the rate of rotation of the screw conveyors and the number of back paddles placed on them were determined by such experiments. This was done in the interest of conserving the much more expensive Co-Ox M and of avoiding the necessity of having to reactivate it following its exposure to air. The above heat transfer experiments, however, showed that Co-Ox M and flour are not similar materials and it was possible therefore that the Co-Ox M was not being transferred at the same rate as the flour. This suspicion was further supported by the fact that the material was not cooled on passage through the oxygenation chamber. Approximately 50 per cent of the heat which must be removed during the oxygenation is derived from the heat of reactivation of the material and this is known to take place in a period of about 8 minutes. It appeared that the material was being moved faster than was originally intended. In order to determine the rate of movement of the material one of the cross conveyors was removed and a tared container placed such that it collected the Co-Ox M conveyed through the chambers as the machine was operated. Approximately 10 pounds of material were moved through the apparatus per minute and since approximately 100 lbs. of material were contained in the apparatus, the circulation through the apparatus required only 10 minutes instead of the 15 minutes which had been originally intended.

The modification of the apparatus is being continued as the experimental results and reason dictate.

Further details concerning this apparatus will be found in Report XXXIV.

APPENDIX I.

SUMMARY OF REPORTS ON OXYGEN PROBLEM

Report No.	Report to NDRC No.	By	Period Covered by Report	Date of Report
Chao 1		Chao and Diehl Cobalt, iron and manganese derivatives of di-salicylalethylenediimine; disalicylalbenzidine cobalt; test for oxygenation capacity; luminescence test.		10-20-38
Chao 2		Chao and Diehl Cobalt, iron, copper, and chromium derivatives of disalicylalethylenediimine; cobalt, iron, and manganese derivatives of disalicylalphenylenediimine; cobalt, iron and manganese derivatives of disalicylalbenzidine.		11-20-38
Chao 3		Chao and Diehl Tin derivatives of disalicylalethylenediimine and disalicylalphenylenediimine; lead disalicylalethylenediimine; effect of nitrogen on disalicylalethylenediimine cobalt; salicylalamide cobalt.		12-20-38
Chao 4-5		Chao and Diehl Reduction of nitroalkanes; purification of salicylaldehyde; Schiff's bases of salicylaldehyde and various alkylamines; cobalt derivatives of the latter; preparation of disalicylalethylenediimine cobalt of high capacity,		3-3-39
Chao 6-7		Chao and Diehl Continuation of work on derivatives of monamines with salicylaldehyde and ammonia; methylamine, ethylamine, n-propylamine, iso-propylamine, n-butylamine, n-amylamine, aniline.		4-28-39
I		Hach and Diehl Constitution of disalicylalethylenediimine cobalt; analysis and molecular weight of disalicylalethylenediimine cobalt; the effect of light on the material; the effect of pressure on oxygenation; apparatus for producing oxygen; preparation; di-(3-nitrosalicylal)ethylenediimine cobalt; di-(5-nitrosalicylal)ethylenediimine cobalt; cobalt	10-1-40 to 2-15-41	2-17-41

Report No.	Report to NDRC No.	By	Period Covered by Report	Date of Report
	derivatives of salicylaldehyde and diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and hydroxyethylethylenediamine; mechanism of the oxygenation process.			
II		Hach and Diehl	2-15-41 to 3-15-41	3-19-41
	Effect of light of various wave lengths on disalicylalethylenediimine cobalt; temperature of deoxygenation; study of synthesis and olive, red, and black by-products; other methods of preparation; presence of water in the compound; the valence of cobalt in the compound; the rate of oxygenation.			
III		Diehl, Hach and Harrison	3-15-41 to 8-25-41	8-27-41
	The rate of oxygenation of disalicylalethyenediimine cobalt at different temperatures and pressures; construction of apparatus; continuous, circulating solid apparatus, batch operation without stirring (stationary bed) with and without recirculation of gases, batch process with stirring using paddle and using rotating drum; explosibility; density; further notes on preparation of large batches; the effect of moisture.			
IV		Diehl, Hach and Harrison	8-25-41 to 11-10-41	11-14-41
	Preparation of disalicylalethylenediimine cobalt; the various methods; effect of the purity of the salicyladehyde, effect of excess of any one of the reactants, effect of the order and rate of addition of reagents, effect of temperature, effect of alcohol concentration, effect of volume of solvent, effect of air, effect of time of standing; effect of cooling; effect of composition of wash liquid; effect of washing; effect of manner of drying; recommended procedures.			
V	1	Hach, Harrison and Diehl	11-10-41 to 1-5-42	1-8-42
	Further studies on preparation of disalicylalethylenediimine cobalt; Harrison-Hach method;			

Report No.	Report to NDRC No.	By	Period Covered by Report	Date of Report
		direct mixing method; analysis of disalicylalethylenediimine cobalt; high temperature drying; dirty brown compound; bright red inactive compound; stereochemical considerations; effect of washing with alcohol and benzene; effect of carbon monoxide, nitric oxide, nitrogen dioxide; the recovery of salicylaldehyde and cobalt.		
VI	2	Henselmeier and Diehl	12-15-41 to 1-2-42	1-7-42
		Ethylenediamine, pyruvic acid and cobalt.		
VII	3	Diehl	1-10-42 to 2-14-42	2-14-42
		Monthly report.		
VIII	4	Harrison and Diehl	1-5-42 to 1-15-42	2-23-42
		Disalicylalpropylenediimine cobalt.		
IX	5	Hach and Diehl	1-42	2-23-42
		Effect of nitrogen dioxide, nitrous oxide, and sulfur dioxide on disalicylalethylenediimine, disalicylalethylenediimine cobalt, and the bright red inactive isomer.		
X	6	Liggett and Diehl	12-15-41 to 1-20-42	2-23-42
		Preparation of disalicylalethylenediimine cobalt by pyridine method; cobalt and iron derivatives of disalicylalphenylenediimine; operation of disalicylalethylenediimine cobalt in solution in pyridine and in chloroform.		
XI	7	Head and Diehl	12-15-41 to 1-23-42	2-23-42
		Tridentate cobalt compounds from o-hydroxybenzalimino-o-phenol.		

Report No.	Report to NDRC No.	By	Period Covered by Report	Date of Report
XII	8	Diehl	2-14-42 to 3-14-42	3-14-42
	Monthly report.			
XIII	9	Henselmeier and Diehl	1-2-42 to 2-14-42	3-9-42
	Cobalt derivatives of pyruvic acid and ethylenediamine, propylenediamine, and o-phenylenediamine.			
XIV	10	Hach and Diehl	2-18-42 to 3-24-42	4-14-42
	Nitration of salicylaldehyde; separation of 3- and 5-nitro isomers; di-(3-nitrosalicylal)-ethylenediimine cobalt; di-(5-nitrosalicylal)-ethylenediimine cobalt.			
XV	11	Head and Diehl	4-6-42 to 4-9-42	4-14-42
	Nitration of salicylaldehyde: variation in nitric acid concentration.			
XVI	12	Liggett and Diehl	1-17-42 to 3-25-42	3-27-42
	3-, 4-, 5-, and 6-methylsalicylaldehydes, their condensation with ethylenediamine and cobalt; di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt; 2-hydroxy-1-naphthaldehyde and its condensation with ethylenediamine and cobalt; study of Reimer-Tiemann reaction.			
XVII	13	Henselmeier and Diehl	2-14-42 to 3-3-42	4-27-42
	Disalicylalethylenediimine cobalt by pyridine method; disalicylalpropylenediimine cobalt by pyridine method; o-hydroxyacetophenone with ethylenediamine and cobalt; resacetophenone; di-(2-hydroxy-3-methoxybenzal)-ethylenediimine cobalt.			

Report No.	Report to NDRC No.	By	Period Covered by Report	Date of Report
XVIII	14	Head and Diehl	2-20-42 to 3-4-42	3-16-42
	Resolution of propylenediamine and disalicylal-l-propylenediimine cobalt.			
XIX	15	Head and Diehl	1-31-42 to 2-10-42	4-14-42
	Disalicylalethylenediimine iron.			
XX	16	Harrison and Diehl	1-1-42 to 2-24-42	
	The magnetic susceptibility of disalicylalethylenediimine cobalt and related compounds.			
XXI	17	Head, Hach and Diehl	2-20-42 to 3-2-42	5-6-42
	Cobalt, salicylaldehyde and decamethylenediamine, nonamethylenediamine, hexamethylenediamins, trimethylenediamine, iso-propylamine, and 2,3-butylenediamine; preparation of disalicylalethylenediimine cobalt; density of disalicylalethylenediimine cobalt, cobaltinitrite method of purifying cobalt.			
XXII	18	Harrison and Diehl	2-19-42 to 2-20-42	4-27-42
	Cobalt, iron and manganese derivatives of ethylenediamine and 3-bromosalicylaldehyde.			
XXIII	19	Diehl	3-14-42 to 4-15-42	4-16-42
	Monthly report.			
XXIV	20	Harrison and Diehl	2-24-42 to 3-29-42	7-20-42
	Preparation of disalicylalethylenediimine cobalt under anhydrous conditions; the green and orange compounds and their conversion with water to oxygen carriers.			

Report No.	Report to NDRC. No.	By	Period Covered by Report	Date of Report
XXV	21	Head and Diehl	3-22-42 to 3-26-42	5-1-42
	2-Hydroxy-3-methoxy-5-nitrobenzaldehyde and ite condeneation with ethylenediamine and eobalt.			
XXVI	22	Diehl	12-1-41 to 4-15-42	4-22-42
	Firet progreee report.			
XXVII	23	Liggett and Diehl	3-26-42 to 5-13-42	5-13-42
	Di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt; preparation by various methode; volumetric determination of oxygen capacity, rate of oxygenation.			
XXVIII	24	Diehl	4-15-42 to 5-13-42	5-13-42
	Monthly report.			
XXIX	25	Head and Diehl	3-17-42 to 5-15-42	
	Nitration of salicylaldehyde; variation of excese nitric acid and of amount of acetic acid; recommended procedure.			
XXX	26	Hach, Head and Diehl		
	Rate of deterioration of diealieylalethylenediimine cobalt and di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt with rotating drum machine.			
XXXI	27	Hach Liggett and Diehl		
	Di-(2-hydroxy-3-nitrobenzal)ethylenediimine cobalt activation, rate of oxygenation at various temperaturee, pressures and humidities, rate of hydration and oxygenation.			

<table>
<tr><th>Report No.</th><th>Report to NDRC No.</th><th>By</th><th>Period Covered by Report</th><th>Date of Report</th></tr>
<tr><td>XXXII</td><td>28</td><td>Hanselmeier and Diehl</td><td>4-1-42 to 5-15-42</td><td>7-15-42</td></tr>
<tr><td></td><td colspan="4">Di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt; synthesis of 2-hydroxy-5-phenylbenzaldehyde by the Duff reaction; synthesis of 2-hydroxy-3-nitro-5-methylbenzaldehyde.</td></tr>
<tr><td>XXXIII</td><td>29</td><td>Diehl</td><td>5-13-42 to 6-15-42</td><td>6-17-42</td></tr>
<tr><td></td><td colspan="4">Monthly report.</td></tr>
<tr><td>XXXIV</td><td>30</td><td>Hach and Diehl</td><td>5-20-42 to 7-23-42</td><td>7-27-42</td></tr>
<tr><td></td><td colspan="4">Circulating solid apparatus.</td></tr>
<tr><td>XXXV</td><td>31</td><td>Schwandt and Diehl</td><td>6-1-42 to 7-25-42</td><td>8-5-42</td></tr>
<tr><td></td><td colspan="4">Tetramethylethylenediamine with cobalt and salicylaldehyde, with 2-hydroxy-3-methoxybenzaldehyde, and with 2-hydroxy-3-nitrobenzaldehyde.</td></tr>
<tr><td>XXXVI</td><td>32</td><td>Harrison and Diehl</td><td></td><td></td></tr>
<tr><td></td><td colspan="4">Differential manometric capacity and rate apparatus; summary of applications.</td></tr>
<tr><td>XXXVII</td><td>33</td><td>Brouns and Diehl</td><td></td><td></td></tr>
<tr><td></td><td colspan="4">Preparation of <u>o</u>-ethoxyphenol; preparation of 2-hydroxy-3-ethoxybenzaldehyde by the Duff reaction; di-(2-hydroxy-3-ethoxybenzal)ethylenediimine cobalt; preparation, activation, rate of oxygenation, hydration and dehydration; demethylation of 2-hydroxy-3-methoxybenzaldehyde; ethylation of 2,3-dihydroxybenzaldehyde; preparation of <u>o</u>-<u>n</u>-propoxyphenol; preparation of 2-hydroxy-3-<u>n</u>-propoxybenzaldehyde; di-(2-hydroxy-3-<u>n</u>-propoxybenzal)ethylenediimine cobalt: preparation, rate of oxygenation, hydration; preparation of <u>o</u>-<u>iso</u>-propoxyphenol; preparation of 2-hydroxy-3-<u>iso</u>-propoxybenzaldehyde.</td></tr>
</table>

Report No.	Report to NDRC No.	By	Period Covered by Report	Date of Report
XXXVIII	34	Liggett, Head, Diehl, Calvin and Co-workers	5-13-42 to 7-24-42	7-24-42
	Di-(2-hydroxy-3-methoxybenzal)ethylenediimine cobalt: additional studies on methods of preparation, large scale preparation, activation apparatus, hygroscopicity and effect on capacity, analysis, magnetic susceptibility (Calvin), rate of oxygenation, rate of deterioration in use, equilibrium pressure (Calvin).			
XXXIX	35	Diehl	6-15-42 to 7-23-42	7-23-42
	Monthly report.			
XL	36	Diehl	7-24-42 to 8-15-42	8-15-42
	Monthly report.			
XLI	37	Head and Diehl	4-24-42 to 5-20-42	
	2-Hydroxy-3-bromobenzaldehyde with ethylenediamine and cobalt.			
XLII	38	Harrison and Diehl	7-22-42 to 8-21-42	
	2,3-Dihydroxybenzaldehyde with ethylenediamine and cobalt.			
XLIII	39	Mathews and Diehl		
	Acetylacetone, benzoylacetone, and dibenzoylmethane with ethylenediamine and cobalt.			
XLIV	40	Mathews and Diehl	5-1-42 to 6-1-42	9-14-42
	Allylamine polynuclear compounds.			

Report No.	Report to NDRC No.	By	Period Covered by Report	Date of Report
XLV	41	Liggett and Diehl	7-11-42 to 8-24-42	9-15-42
	2-Hydroxy-3-nitro-5-methylbenzaldehyde with ethylenediamine and cobalt;formylcamphor with cobalt and ethylenediamine and with o-phenylenediamine; methylenediamine with salicylaldehyde and cobalt.			
XLVI	42	Diehl	4-15-42 to 9-1-42	
	Second progress report.			
XLVII	43	Head and Diehl		
	2,4-Dihydroxybenzaldehyde, 2-hydroxy-4-methoxybenzaldehyde,2,5-dihydroxybenzaldehyde, 2-hydroxy-5-methoxybenzaldehyde, and 2-hydroxy-5-ethoxybenzaldehyde: their condensation with ethylenediamine and the cobalt derivatives.			
XLVIII	44	Harrison and Diehl		
	3-Alkoxy compounds.			
XLIX	45	Diehl	8-15-42 to 9-15-42	9-15-42
	Monthly report.			

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ABSTRACT:

A summary is presented of the chemical investigations of the regenerative oxygen absorbent Salcomine and the synthesis and properties of related chemical compounds. The cobalt compound derived from 2-hydroxy-3-methoxy-benzaldehyde and ethylenediamine was found to carry oxygen and to oxygenate at a rate approximately 20 times that of the parent compound. This compound was obtained in the form of a hydrate which was converted into the active form by heating in a vacuum at 170°. An extensive study of six methods for the preparation of this compound was made, and it was found that the most satisfactory method was that involving the precipitation of the cobalt derivative from a solution of the sodium salt of the Schiff's base in dilute alcohol.

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23

* Oxygen Compounds
Cobalt Compounds